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JOURNAL

OF

THE CHEMICAL SOCIETY

I.—*On Sparteine.*

By E. J. Mills.

The formula of Sparteine, the volatile base discovered by Stenhouse,* in *Spartium scoparium,* has long been a matter of doubt among chemists. Stenhouse assigns to this substance the composition—

$$C_{15}H_{13}N‡$$

which expression cannot be represented if the carbon-equivalent ($C=12$) be adopted. To avoid this difficulty, Gerhardt† proposed the formula—

$$C_{16}H_{13}N,‡$$

which offered a tolerable approximation to the analytical results of Stenhouse, without, however, deciding the question by an appeal to experiment. The opinion of this illustrious chemist, so often tried and found correct in similar cases, has, very naturally, been accepted in most Manuals. Nevertheless, the point remained unsettled; and it appeared of some interest to gain additional experimental eivdence for the final elucidation, not only of the formula, but also of the constitution of sparteine. Some results which I have obtained in this direction, are recorded in the following paragraphs:

In preparing this substance, I have essentially followed the process devised by Dr. Stenhouse. The plant was simply exhausted with water faintly acidulated with sulphuric acid. The extract was then evaporated to a smaller bulk, and distilled with caustic soda until the distillate ceased to exhibit a bitter taste or an alkaline re-action. On evaporating the distillate, mixed with hydrochloric acid, to dryness on the water-bath, and distilling the mass with solid hydrate of potassium—the mixture being just moistened at the commencement—the thick, oily base passed over into the receiver,—long preceded, of course, by the ammonia invariably present. The substance was then gently heated with sodium, in a current of dry hydrogen gas, by which means all the water was removed. (It deserves to be noticed that no other mode of drying succeeded; even exposure *in vacuo* for twenty-four hours, with metallic sodium, failed to dehydrate the base.) The sparteine was now freed from the sodium and again distilled, the assistance of the current of hydrogen being this time dispensed with. 150lbs. of the plant yielded about 22 cub. cent. of base.

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* Stenhouse, Ann. Ch. Pharm. (1851), lxxviii, 15.

† Gerhardt. Chim. org. iv, 236.

‡ ($C = 6$, $O = 8$, &c.)

I need not recapitulate the properties of this substance, already so well described by Stenhouse. If its high boiling point be considered, the idea naturally suggests itself to attribute a diammonic character to sparteine. This circumstance, together with the odour, the well-defined narcotic action, and other properties, tempted me to hope that it would prove homologous with nicotine. In fact, if Gerhardt's formula be doubled, the homology of the two substances, which are so closely allied in their chemical characters, becomes at once apparent.

Nicotine, $C_{10}H_{14}N_2$* Sparteine, $C_{16}H_{26}N_2$.

In this hope, however, I was disappointed, as will be seen from the following numbers :—

I. 0·32475 grm. substance, burnt with oxide of copper, gave 0·91525 grm. carbonic acid and 0·33375 grms. water.

II. 0·4225 grm. substance, again distilled and similarly treated, gave 1·18675 grm. carbonic acid, and 0·43625 grm. water.

	I.	II.
Carbon . .	76·86	76·86
Hydrogen .	11·42	11·47
Nitrogen .	„	„

These results are so closely coincident with those of Dr. Stenhouse that they may be fairly assumed to represent the composition of sparteine, which would thus become a diamine, containing—

---

* C = 12, &c., et seq.

$$C_{15}H_{26}N_2$$

a formula which is unequivocally supported by its deportment with iodide of ethyl.

The following table shows the theoretical values of Gerhardt's and Stenhouse's formulæ, together with the means of the analytical results obtained by Stenhouse and myself respectively:

Gerhardt's Formula (doubled).		Stenhouse's Formula (doubled).		Stenhouse. (Analysis).	Mills. (Analysis).
C_{16}	78·05	C_{15}	76·92	76 69	76·86
H_{26}	10·57	H_{26}	11·11	11·09	11·44
N_2	11·38	N_2	11·97	„	„

Salts of Sparteine.

Some of these salts are uncrystallizable, while others are easily obtained in crystals.

The *chloride, bromide,* and *iodide* are amorphous, of a resinous character, and unfit for analysis.

The *oxalate* I obtained by neutralizing the aqueous solution of the base with oxalic acid and evaporating. The crystals were of acicular form, and difficult to obtain.

For additional corroboration of the formula of sparteine, I have examined several of its double-salts.

Platinum-salt.—This salt is precipitated as a yellow crystalline powder, when a solution of dichloride of platinum is added to a solution of sparteine in hydrochloric acid. It may be readily purified by solution in hot hydrochloric acid, filtering, and recrystallizing. With care, large crystals, having very brilliant faces, may be obtained. Analysis furnished the following numbers:—

I. 0·475 grm. substance, dried *in vacuo,* gave, on combustion, 0·459 grm. carbonic acid, and 0·2105 grm. water.

II. 0·613 grm. same substance, similarly dried, gave, on ignition, 0·176 grm. platinum.

III. 0·4795 grm. substance, similarly dried, gave, on combustion, 0·4795 grm. carbonic acid, and 0·2280 grm. water.

IV. 0·45175 grm. substance, dried at 100°, gave, on ignition, 0·1317 grm. platinum.

V. 0·34750 grm. substance, dried at 100°, gave, on ignition, 0·10250 grm. platinum.

These numbers lead to the formula—

$$C_{15}H_{26}N_2.2HCl.2PtCl_2+2H_2O$$

the theoretical values of which I place in juxtaposition with the experimental percentages:—

	Stenhouse.				Mills.				
	I.	II.	III.	IV.	I.	II.	III.	IV.	V.
Carbon .	26·55	26·33	„	„	26·35	„	27·01	„	„
Hydrogen	4·99	4·74	„	„	4·92	„	5·28	„	„
Platinum	29·02	28·63	28·73	28·75	„	28·71	„	29·16	29·49

		Theory.	
C_{15}	=	180·00	26·38
H_{32}	=	32·00	4·69
N_2	=	28·00	4·11
Cl_6	=	213·00	31·22
Pt_2	=	197·40	28·91
O_2	=	32·00	4·69
		682·40	100·00

The *Gold-salt* was prepared, but not analysed, by Stenhouse. I have obtained this salt with all the properties assigned to it by its discoverer.

0·188 grm. substance gave, on ignition, 0·0605 grm. gold = 32·18 per cent. This number agrees with the formula—

$$C_{15}H_{26}N_2.2HCl.AuCl_3$$

which requires 32·27 per cent.; and thus it is seen that the hydrochlorates of the diamines are capable of combining, either with one or with two equivalents of a metallic chloride.

I have also prepared the *zinc-iodide* and *zinc-chloride* of sparteine. They are readily obtained by gently heating a solution of sparteine with hydriodic acid and iodide of zinc, or with hydrochloric acid and chloride of zinc.

Iodide of Zinc and Sparteine.—This salt crystallizes in fine needles, which are apt to become brown on exposure to air. I have only determined the iodine in this salt.

0·366 grm. substance, dried *in vacuo,* and precipitated with nitrate of silver, gave 0·4225 grm. of iodide of silver = 62·39 per cent. iodine. The formula—

$$C_{15}H_{26}N_2.2HI.2ZnI$$

requires 62·78 per cent.

Chloride of Zinc and Sparteine.—This salt crystallizes in magnificent needles, which I have obtained half an inch long. They are white, somewhat hard, and lustrous. The composition of this salt is probably

$$C_{15}H_{26}N_2.2HCl.2ZnCl.$$

Action of Iodide of Ethyl on Sparteine.

The process of ethylation, unknown at the time when sparteine was first prepared, has proved of the greatest service in establishing the constitution of this base.

When equal volumes of sparteine, ordinary methylated spirit, and iodide of ethyl, are heated together for about an hour, in sealed tubes, at 100° C., the mixture assumes a dark colour, and deposits abundance of crystals of an ethylated compound,—sparingly soluble in cold, readily soluble in hot alcohol, and excessively soluble in water. Well-washed with cold, and once recrystallized from hot alcohol, the substance was obtained pure, and gave the following analytical results:—

I. 0·5010 grm. substance* gave, on combustion with a mixture of chromate of lead and oxide of copper, 0·7275 grm. carbonic acid, and 0·2895 grm. water.

II. 0·4550 grm. substance, similarly treated, gave 0·6505 grm. carbonic acid, and 0·2635 grm. water.

III. 0·5135 grm. substance, gave, on precipitation with nitrate of silver, 0·4656 grm. iodide of silver.

IV. 0·31525 grm. substance gave, on similar treatment, 0·2861 grm. iodide of silver.

These numbers represent the formula

$$C_{17}H_{32}N_2I_2 = [C_{15}H_{27}(C_2H_5)N_2]''I_2,$$

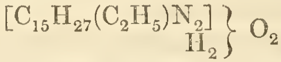
---

* The substance was in each analysis, dried in vacuo.

as may be seen from the following comparison of the theoretical values with the experimental percentages :—

	Theory.			Experiment.			
			I.	II.	III.	IV.
C_{17} =	204	39·38	39·60	38·99	„	„
H_{32} =	32	6·18	6·42	6·43	„	„
N_2 =	28	5·40	„	„	„	„
I_2 =	254	49·04	„	„	49·00	49·04
	518	100·00				

The formation of this compound proves most satisfactorily the diammonic nature of sparteine.* The iodide crystallizes in the form of long needles, beautifully grouped, and radiating from a centre. Treated with a boiling solution of potash, this salt remains unaltered; oxide of silver, however, rapidly transforms it, when in aqueous solution, into the powerfully alkaline hydrated oxide—



$$\left.\begin{array}{r}[C_{15}H_{27}(C_2H_5)N_2]\\ H_2\end{array}\right\}O_2$$

the composition of which was confirmed by the analysis of its *platinum-salt*. This was prepared by treating the iodide with chloride of silver, and the chloride thus produced with dichloride of platinum, in the *cold*. In this manner, a semi-crystallized precipitate was obtained, soluble in water, alcohol, and more readily in hydrochloric acid. Dried *in vacuo* over sulphuric acid :

0·227 grm. substance gave, on ignition, 0·066 grm. platinum, corresponding to 29·07 per cent. The formula

$$C_{17}H_{32}N_2Pt_2Cl_6 = [C_{15}H_{27}(C_2H_5)N_2]Cl_2.2PtCl_2$$

requires 29·26 per cent.

---

* Note. In the above reaction between iodide of ethyl and sparteine, a secondary product is found, in very small quantity, in the alcholic washings from the monoethylated di-iodide. The substance is white, excessively soluble in alcohol, almost insoluble in cold, sparingly soluble in hot water. Crystallized from the latter solvent, it appears in the form of small, well-defined, almost square rhombohedral crystals. I determined the iodine in this substance, as well as the platinum in the platinum-salt obtained from it; the numbers were respectively 36·25 per cent. (I), and 27·95 per cent. (Pt). It will be perceived that these numbers present a mutual discrepancy; and I much regret that I was unable to procure sufficient substance for a determination of the carbon and hydrogen.

The *dichloride* corresponding to the mono-ethylated di-iodide, is less easy to obtain, and crystallizes also in needles. It forms, with chloride of zinc, a beautiful acicular double salt, easy to crystallize.*

Action of Iodide of Ethyl on Ethyl-Sparteine.

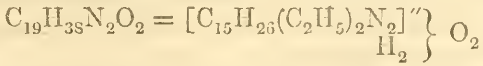
When the hydrate of this base, obtained by the action of oxide of silver on the iodide, is digested with alcohol and iodide of ethyl in sealed tubes, at 100° C., for a short period, there is obtained, on evaporation of the liquid, a crystalline iodide, always contaminated with free iodine, which differs essentially from the iodide of the mono-ethylated base. If the evaporation be conducted in a stream of sulphuretted hydrogen gas, the separation of much of the iodine is effected, and the substance rendered considerably purer. The new iodide crystallizes from alcohol in short minute crystals, and is very soluble in water. Treated with oxide of silver, it yields a powerfully alkaline solution. Boiled with chloride of silver, the iodide is converted into the corresponding chloride, which is deliquescent, and not easy to obtain in crystals. The latter, treated with dichloride of platinum, furnishes a very voluminous platinum-salt of light yellow colour, and crystallizing in radiated aggregations from its solution in weak alcohol. It is very soluble in water; a mixture of alcohol and ether fails to precipitate it entirely. On analysis,

0·213 grm. substance gave, by ignition, 0.0610 grm. platinum = 28·64 per cent.

Want of material here prevented me from performing these experiments on a more extensive scale. The natural interpretation of the above observations would be to assume that the action of iodide of ethyl upon the mono-ethylated sparteine produces the di-ethylated iodide—

$$C_{19}H_{36}N_2I_2 = [C_{15}H_{26}(C_2H_5)_2N_2]''I_2,$$

which, with oxide of silver, yields the caustic hydrate of the diammonium—



$$C_{19}H_{38}N_2O_2 = \left.\begin{matrix}[C_{15}H_{26}(C_2H_5)_2N_2]'' \\ H_2\end{matrix}\right\} O_2$$

---

* Compare Dr. Hofmann's "Notes of Researches on the Poly-ammonias." No. XIV. "Diagnosis of Diamines."—Proceedings of Royal Society, vol. xi, p. 278.

furnishing, lastly, by treatment with hydrochloric acid and dichloride of platinum, the platinum-salt—

$$C_{19}H_{36}N_2Pt_2Cl_6 = [C_{15}H_{26}(C_2H_5)_2N_2]''Cl_2.2PtCl_2.$$

This formula requires 28·10 per cent. of platinum. The analysis above gives as much as 28·64 per cent. The salt was probably still contaminated with a minute proportion of the mono-ethylated compound.

The results of this inquiry prove unmistakably that sparteine is a tertiary diamine of the formula

$$C_{15}H_{26}N_2 = (C_{15}H_{26})^{vi}N_2.$$

Further investigation is necessary to afford some insight into the nature of the complex atom $(C_{15}H_{26})^{vi}$ which assumes the place of six equivalents of hydrogen.

The above experiments on sparteine were carried out in Dr. Hofmann's laboratory.

II.—*On the occurrence of deposits of Crystallised Phosphate of Lime in Human Urine.*

By H. Bence Jones, M.D., F.R.S., F.C.S.

In March, 1861, Dr. William Roberts, Physician to the Manchester Royal Infirmary, published a paper, in the British Medical Journal, on the occurrence of deposits of crystallised phosphate of lime in human urine. He says:—"By adding a little chloride of calcium to healthy urine, and reducing its acidity to near the neutral point with caustic soda, I have often succeeded in obtaining an abundance of crystals, closely resembling those occurring spontaneously in urine."

At this date I had satisfied myself, that healthy urine, out of the body, could be made to give crystals of phosphate of lime, first, by simply adding chloride of calcium to the urine; secondly, by taking away some of the acidity of the urine; thirdly, by both means simultaneously.

When the fluid was very acid, much chloride of calcium was required to be added; but if a portion of the acid was removed in any way, then less chloride of calcium was required to produce crystals of phosphate of lime.

These experiments made me believe, that, by giving a lime-salt internally, phosphate of lime crystals ought to be found in the urine, even without adding anything to the water after it was made.

A long delay occurred before I could begin the observations in St. George's Hospital, and ultimately I was obliged to ask my friend, Dr. Dickenson, to undertake the microscopical examination of the urine of those to whom the lime-salt was given.

Although, therefore, these experiments were ended long after Dr. Roberts' publication, yet, as the observations recorded in the first part of this paper, were made without any knowledge that he was experimenting on the same subject, our agreement must be considered as accidental, and may therefore be taken as the better evidence of the truth of our facts.

PART 1. *On the production of crystals of Phosphate of Lime in the Urine, by the addition of substances after it has been passed.*

IT appeared desirable to determine the circumstances and form in which crystallised phosphate of lime occurred, when pure solutions of chloride of calcium, and common phosphate of soda, or acid phosphate of soda were mixed together.

When a solution of chloride of calcium in excess is precipitated by a solution of common phosphate of soda, the precipitate, when examined by the microscope, is seen to be partly amorphous and partly crystalline. The amorphous precipitate, according to Heintz, is $3CaO.\ PO_5$, and the crystalline $2CaO.HO.PO_5$.

When a solution of common phosphate of soda, in excess, is precipitated by solution of chloride of calcium, the precipitate, examined by the microscope, is amorphous.

If a little acetic acid is first added to the solution of common phosphate of soda, and then the solution of chloride of calcium, an amorphous precipitate is first seen, and this, more or less rapidly (in the course of half an hour) becomes entirely crystalline. When lactic acid, butyric acid, valeranic acid, or very weak hydrochloric acid was used instead of acetic acid, the same crystals were observed after a short time. If an excess of these acids was used, no crystals were formed.

When a solution of chloride of calcium in excess was added to a solution of acid phosphate of soda, crystals of phosphate of lime were found by the microscope, in from ten to fifteen minutes.

When there was much acid phosphate, in proportion to the chloride of calcium, the crystalline deposit was always found.

It was clear then that crystalline phosphate of lime was formed, if sufficient lime-salt was present, and if the acid was not in such excess as to keep the salt dissolved.

As the urine always contains common phosphate of soda or acid phosphate of soda, with or without free acid, and with variable quantities of lime-salt, experiments were made to obtain crystalline phosphate of lime, 1st, by increasing the lime-salt by adding chloride of calcium; or, 2ndly, by diminishing the acidity of the urine by cautious additions of alkali, so as to allow the lime-salt naturally present to crystallise out; or, 3rdly, by increasing the lime-salt, and diminishing the acidity of the urine at the same time. In each of these ways, crystals of phosphate of lime were obtained.

1st. By simply adding chloride of calcium to healthy urine.

To 50 c. c. of urine, a few drops of a strong solution of chloride of calcium were added, until a slight precipitate was obtained. The precipitate that formed, was first amorphous, but half an hour afterwards, beautiful crystals of phosphate of lime were seen by the microscope. If a great excess of chloride of calcium was added, the precipitate was almost entirely amorphous.

Thirteen different experiments were made with different healthy urines from two men, chloride of calcium in solution was added, and in each case, crystals of phosphate of lime were found in from half an hour to an hour.

2ndly. Crystalline phosphate of lime was obtained from healthy urine, by diminishing the acidity of the urine by the cautious addition of alkali.

To 30 c. c. of healthy urine, a quantity of ammonia was added, not sufficient to produce a precipitate. After standing 12 hours, no crystals of phosphate of lime could be found with the microscope.

To 30 c. c. of urine, ammonia was added, so that the urine had a feebly acid reaction. The precipitate which formed, appeared, when examined by the microscope, to consist chiefly of crystallised phosphate of lime.

To 30 c. c. of urine, so much ammonia was added, as gave a neutral reaction. Besides crystals of phosphate of ammonia and magnesia, crystals of phosphate of lime were formed.

In another experiment, the urine was made alkaline; the precipitate then consisted of phosphate of ammonia and magnesia, and amorphous phosphate of lime.

Solution of common phosphate of soda, and solution of potassa also, when added to healthy urine, occasionally gave, on standing for some time, crystals of phosphate of lime.

3rdly. By increasing the lime-salt, and diminishing the acidity of the urine at the same time, crystalline phosphate of lime was produced.

Four specimens of healthy urine gave with chloride of calcium, no precipitate. Solution of potassa was then added in small quantity till a slight precipitate was observed; the urine still had a slightly acid reaction; on examination with the microscope from half an hour to an hour afterwards, crystals of phosphate of lime were found.

In two other cases, some of the acidity was removed by potassa, and solution of chloride of calcium was then added; the precipitate, when examined with the microscope, contained crystals of phosphate of lime.

In another case in which chloride of calcium gave no precipitate at all, the urine was mixed with a little ammonia to take away the greater part of the acid present, and then a solution of chloride of calcium was added. The precipitate contained crystals of phosphate of lime.

That it is not necessary to lessen the acidity of the urine, provided the phosphate of lime is in great excess, is proved by the following experiments:—

To 50 c. c. of healthy urine, a few drops of, 1st, dilute acetic, or 2ndly, lactic acid, were added, and then so much of a solution of chloride of calcium as caused only a slight precipitate. After standing some hours, the precipitate, which was at first amorphous, was changed in both cases into beautiful crystals of phosphate of lime.

Hence—

The two chief conditions, which need not co-exist, on which the formation of crystalline phosphate of lime in the urine depends, are—

1st. An excess of phosphate of lime; and

2ndly. A slight acidity of the urine, in which the phosphate of lime is dissolved.

Part 2.—*On the production of Crystals of Phosphate of Lime in the urine by giving preparations of lime as medicine.*

The ease with which crystals of phosphate of lime were obtained after any urine was passed, by adding substances to the urine, led me to expect, that by giving lime-salts as medicine, phosphate of lime crystals would, with equal readiness, be detected in the urine.

I soon found that it was not so easy to affect the composition of the urine before it passed from the body, and that careful collecting, and watching for many hours afterwards, was required to arrive at clear results.

My friend, Dr. Dickenson, undertook the microscopical examination of the urine in the wards of St. George's Hospital, where I ordered the preparations and quantities of the medicine which I wished to try.

At first, acetate of lime with lime-water, and sometimes with carbonate of potassa, to reduce the acidity of the urine, were tried. Then lime-water alone, or carbonate of lime was used; but ultimately a solution of acetate of lime, containing about 15 grains to a drachm of solution, gave the best results.

As examples of our first experiments, we give the following,—

E. P., æt. 22, admitted May 15, 1861, for dyspepsia. He was nearly leaving the hospital well, and the urine was healthy, and in all respects natural, when he was ordered, June 1st, 2 drachms of solution of acetate of lime, in water every six hours, (each drachm contained 14·7 grains of acetate of lime). The urine which was passed at night and morning was repeatedly examined, after standing for various periods, but nothing but a few crystals of oxalate of lime was observed.

On the 4th, eight ounces of lime-water were given in the day, instead of the acetate.

On the 6th, still only oxalate was found. The lime-water was increased to a pint.

On the 8th, a drachm of carbonate of potassa in addition was given.

On the 11th, no change having been observed, the morning urine was faintly acid; and the surface was covered with an iridescent plate of phosphate of lime. The evening urine was faintly acid when passed, and no crystals of phosphate of lime were found at first. It was again examined forty hours afterwards;

it was then alkaline, and a white precipitate had fallen, which consisted of a considerable quantity of amorphous phosphate, with a great number of very characteristic crystals of phosphate of lime. The surface was covered with a phosphatic pellicle.

12th and 13th, morning and evening. No crystals of phosphate.

14th. Morning urine alkaline, with phosphatic pellicle, and much deposit, consisting chiefly of amorphous phosphate, with a few stellate crystals of phosphate of lime.

14th, evening urine. Eighteen hours after it was passed, no deposit was found; on the third day, many stellate crystals of phosphate of lime were found.

The experiment was continued until the 20th; phosphate of lime crystals occasionally, but by no means constantly, appearing; oxalate of lime was always detected when the urine was acid.

H. E., æt. 30, admitted May 15th for dyspepsia.

June 1st. The urine was in all respects natural; he drank a pint of lime-water during the day.

June 2nd. A few crystals of phosphate of lime were found.
„ 3rd. No phosphate of lime; some oxalate.
„ 4th. No phosphate of lime crystals were found.

In more than one case, carbonate of lime was given in considerable quantity, but no crystals of phosphate of lime were detected in the urine; but the results with acetate of lime, in large doses, were very decided and very uniform, for example,—

S. K., æt. 24. admitted with chronic rheumatism, July 10.

July 20. The urine was perfectly natural, except a small quantity of pus cells, the result of a gonorrhœa.

He was ordered two drachms of solution of acetate of lime equal to 29·4 grains, in water three times daily.

The urine was examined night and morning, and no crystals, except a few oxalate of lime octahedra, were seen, until—

23rd evening. The urine was faintly acid, with an iridescent pellicle on the surface, and a heavy white precipitate formed, which consisted of amorphous phosphate, oxalate of lime, and very numerous characteristic crystals of phosphate of lime. Three drachms of the solution of acetate of lime were ordered thrice daily.

24th morning. Urine faintly alkaline; amorphous and laminar phosphate of lime were seen, but no crystals of phosphate of lime.

24th evening. Urine acid; very large crystals of oxalate were seen; no phosphate. Four drachms of the solution of acetate of lime were ordered.

25th morning. The urine was acid, and showed a few phosphate crystals.

25th evening. The urine was acid, and showed a large deposit of octahedra, but no phosphate.

26th morning. The urine was acid, but showed no crystals.

26th evening. The urine was very faintly acid; numerous fine crystals of phosphate of lime were found.

July 27, morning. The urine was faintly acid; crystalline phosphate of lime was seen, and much oxalate. The acetate of lime was ordered to be stopped, and only three doses were taken between the 27th of July and the 3rd of August; during which time, crystals of phosphate of lime were only twice found by the microscope.

August 2. Morning urine slightly acid; no phosphate crystals.

,, Evening urine acid; much oxalate but no phosphate. Three drachms of the solution of acetate of lime were ordered in water.

3rd. Night water alkaline; few small phosphate of lime crystals were found.

4th. Morning urine alkaline, and few phosphate of lime crystals were found.

4th. Evening urine alkaline; abundant and splendid crystals of phosphate of lime.

5th. Morning urine faintly acid. Phosphate of lime crystals were found; the experiment was stopped.

L. B., æt. 26, admitted with slight rheumatism, July 10.

July 23. The urine was acid and perfectly natural, except that it contained a quantity of pus cells, the result of gonorrhœa.

Two drachms of solution of acetate of lime equal to 29·4 grains, were given thrice daily. The urine was examined night and morning: no crystals were seen until

24th evening. Urine faintly acid; a few needles of phosphate of lime were found, and much amorphous phosphate.

25th. Three drachms of the solution were ordered, but no more crystals of phosphate of lime were seen until

27th morning. The urine, after standing 48 hours, gave many fine bundles of phosphate of lime crystals.

27th evening. Urine gave much oxalate, but no phosphate.

28th morning. Urine faintly alkaline; gave many fine crystals of phosphate of lime.

28th evening, and 29th morning. The urine was not kept.

29th evening to 31st. When the acetate of lime was omitted, no crystalline phosphate was found.

August 3. Three drachms of the solution were again given thrice daily.

No crystals were found until the evening of the 7th, when the urine was acid, and many phosphate of lime crystals were seen.

Four drachms of the solution were ordered, but the patient disliking the medicine, the experiment was stopped.

C. W., æt. 30, was admitted with chronic rheumatism, July 10.

July 30. The urine was acid and perfectly natural, excepting that occasionally a little bladder epithelium was seen.

Three drachms of the solution of acetate of lime were ordered thrice daily, in water. Nothing was observed until

August 3. Morning urine faintly acid; some decided aggregations of phosphate of lime crystals were seen with microscope.

August 3rd, evening. Urine acid but no deposit.

,, 4th, morning. The urine was acid, and showed much oxalate of lime, but no phosphate.

The medicine had to be omitted, in consequence of an increase of rheumatism.

Conclusion.

From the experiments detailed in this paper, it follows that the formation of phosphate of lime crystals in the urine, does not depend upon the amount of phosphoric acid present, but that it does depend, firstly, on the amount of lime in the urine; and secondly, on the acidity of the urine allowing the crystallization to occur.

The increase of lime in the urine, or the diminution of the acidity of the urine, or the simultaneous occurrence of both of these conditions, does not indicate any diseased condition of the body, but may be caused by medicines or by diet.

III.—*Supplementary Note to a Memoir on the power ascribed to the Roots of Plants of rejecting poisonous or abnormal substances presented to them.*

By Charles Daubeny, M.D., F.R.S., M.R.S.A., Foreign Associate of the Royal Academy of Munich, and Professor of Botany, Oxford.

In a memoir read before the Chemical Society in May last, and, since published in the Society's Journal,* I intimated my intention of continuing the researches begun last year, "On the power ascribed to the roots of plants, of rejecting poisonous or abnormal substances presented to them;" and as in the experiments therein detailed, the foreign ingredients had been applied to the plants after they had sprung from the ground, in the liquid form, by watering them with the solution, and it was conceivable that some small portion might have adhered to their external surfaces, although none was actually absorbed by the roots,—I this year endeavoured to avoid that source of error, by introducing the salt into the soil before the seed was sown.

The abnormal substances tried were, as before, the earths strontia and baryta in combination with nitric acid,—and the metal arsenic, which, however, was applied, not in the form of arsenious, but of arsenic acid, which latter, being isomorphous with phosphoric acid, might, it was conceived, be substituted for it in the organism of a plant, and thus become assimilated more readily than arsenious acid.

The crops tried were, as on the former occasion, barley and turnips, and in neither of the two did any very marked difference in the quantity of the crops obtained, arise from the application of the salt. If any thing, the advantage seemed to be rather on the side of those portions of the field which had been thus treated.

The crops were severally examined in the same manner as those of the year preceding had been; but in no one of the six cases, three being the samples of turnips tried with arsenic, baryta and strontia, and three, those of barley treated with the same substances, did any indications of the poisonous or abnormal ingredient which had been introduced into the soil, manifest themselves in the resulting crop.

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* Vol. xiv, p. 209.

I consider these results as rather more conclusive than those obtained in the preceding year, because the substance experimented with, being incorporated with the soil before the seed had been sown, could hardly fail to get into contact with the roots at some part or other.

The only question that can arise is, whether the quantity administered was in each case sufficient to become appreciable in the plants that had grown in contact with it. In the case of the arsenic, I hardly know how this point could be determined more fully, as a larger dose of the poison would be fatal to the vitality of the plant, and thus the very conditions of the problem would be vitiated. With regard, however, to the strontia and baryta, where this objection does not seem to exist, it might be well to settle the point more conclusively, by trying whether the earth would be taken up when quantities of either, larger than were this year employed, had been introduced into the soil.

IV.—*On Piperic and Hydropiperic Acids.*

By G. C. Foster, B.A.

Piperic acid was first described in 1857 by v. Babo and Keller.[*] Their analyses led them to represent its composition by the formula $C_{26}H_{12}O_8$, $C_{50}H_{24}O_{16}$, or $C_{50}H_{22}O_{16}$: the last formula they considered the most probable. The analysis of the acid and of its silver-salt was soon afterwards repeated by Strecker[†], who gave the formula $C_{24}H_{10}O_8$ for piperic acid, and the formula $C_{24}H_9MO_8$ for the piperates, and showed that many of Babo and Keller's own analyses agreed with these expressions. If the accuracy of Strecker's formula be admitted, it seems to indicate that piperic acid is a triatomic acid analogous to glyceric acid, $C_3H_6O_4$ [‡]; otherwise it is difficult to reconcile its monobasic character with the high proportion of oxygen it contains. These considerations induced me to make a few experiments on piperic acid, in the hope of obtaining some knowledge of the relation in which it stands to bodies whose constitution is better understood.

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[*] J. pr. Chem., lxxii, 53; Jahresber., 1857, p. 413.

[†] Ann. Ch. Pharm., cv, 317; Jahresber., 1857, p. 414.

[‡] Here, and hereafter in this paper, $C = 12$, $H = 1$, $O = 16$.

The piperic acid employed was obtained by decomposing piperine with alcoholic potash, according to Babo and Keller's process; but I found that by employing a closed vessel, in which the materials could be heated above the boiling point of alcohol, much time might be saved: 100 grms. piperine, mixed with an equal weight of solid potash and as much strong alcohol as will dissolve both, is completely decomposed when heated for five or six hours to 100°C.

The analysis of piperic acid and of its potassium- and barium-salts gave me numbers which agree with Strecker's formula, as is shown by the following statement of results.

Piperic acid, $C_{12}H_{10}O_4$.

0·517 grm. acid gave 1·248 grm. carbonic acid and ·229 grm. water.

·443 grm. acid gave 1·074 grm. carbonic acid and ·197 grm. water.

	Calculated.		Found.	
C_{12}	144	66·05	65·83	66·12
H_{10}	10	4·59	4·92	4·94
O_4	64	29·36	„	„
$C_{12}H_{10}O_4$	218	100·00		

Piperate of potassium, $C_{12}H_9KO_4$.

0·4371 grm. salt gave ·147 grm. sulphate of potassium.

·425 grm. salt gave ·144 grm. sulphate of potassium.

·7325 grm. salt gave 1·502 grm. carbonic acid and ·232 grm. water.

	Calculated.		Found.		
C_{12}	144	56·25	„	„	55·92
H_9	9	3·52	„	„	3·52
K	39	15·23	15·08	15·19	„
O_4	64	25·00	„	„	„
$C_{12}H_9KO_4$	256	100·00			

Piperate of barium, $C_{12}H_9BaO_4$.—This salt was prepared by adding chloride of barium to a solution of piperate of potassium, and purified by crystallization from boiling water, in which it is somewhat more soluble than in cold water, and subsequent washing with boiling alcohol. A current of carbonic acid passed through a solution of this salt in hot water, decomposes it into carbonate of barium and piperic acid. Air-dry, it does not lose weight at 100°.

0·3082 grm. salt gave ·1251 grm. sulphate of barium.
·3406 grm. salt gave ·1388 grm. sulphate of barium.

	Calculated.	Found.	
Barium per cent. . .	23·99	23·86	23·98

My first experiment with piperic acid was an attempt to reduce it by means of hydriodic acid, in the hope of obtaining a monatomic acid ($C_{12}H_{10}O_2$) which should bear the same relation to it as propionic acid ($C_3H_6O_2$) bears to glyceric acid ($C_3H_6O_4$). In this attempt I was unsuccessful. At 100° C., and even below, piperic acid is converted by hydriodic acid into a black, uncrystallizable substance, carbonic acid being formed at the same time, but no iodine set free. The only crystalline substance which I succeeded in separating from the black carbonaceous product of this reaction, was a small quantity of what appeared to be unaltered piperic acid.

Having failed to reduce piperic acid by hydriodic acid, I hoped to be more successful in employing nascent hydrogen. This reagent, however, instead of giving a product containing less oxygen, gives rise to a new acid containing two atoms of hydrogen more than piperic acid, which I have named *hydropiperic acid.* This substance is best obtained by allowing sodium-amalgam to act for some hours upon a solution of piperate of potassium, kept at a gentle heat, and frequently stirred. The piperate of potassium, which is obtained as a direct product of the action of alcoholic potash on piperine, may be employed for this preparation, after having been once recrystallized. The hydropiperic acid is separated from the alkaline solution by the addition of hydrochloric acid, in the form of oily drops, which gradually solidify when allowed to stand. It may be purified by solution in a large quantity of boiling water, which deposits it on cooling in exceedingly thin, silky needles, sometimes as much as an inch long; or by solution in alcohol, and treatment of the solution with animal charcoal.

Pure hydropiperic acid is colourless; it melts at 63° or 64°C., and solidifies at about 56°; it may sometimes be cooled still lower without solidifying, but then solidifies suddenly when touched with a glass rod; it does not appear to be volatile without decomposition, but when heated in a test-tube it creeps up the sides of the tube, leaving only a very slight residue at the bottom. It is very slightly soluble in cold water, but sufficiently so to give a faint acid reaction to the solution, and to cause it to give a precipitate with acetate of lead; it is somewhat more, but still only sparingly, soluble in hot water, and gives a solution having a strong acid reaction. It separates on cooling, partly as an oil, partly in very fine crystals. Alcohol dissolves hydropiperic acid in all proportions; in ether, also, it is very soluble, and it crystallizes by the spontaneous evaporation of its ethereal solution, in large, but confusedly formed, hard crystals, apparently belonging to the monoclinic system, and many of them hemitropic.

0·1724 grm. acid gave ·4124 grm. carbonic acid and ·0877 grm. water.

·4885 grm. acid gave 1·1715 grm. carbonic acid and ·2495 grm. water.

·466 grm. acid gave 1·116 grm. carbonic acid and ·235 grm. water.

	Calculated.		Found.		
C_{12}	144	65·46	65·24	65·44	65·31
H_{12}	12	5·45	5·65	5·67	5·60
O_4	64	29·09	,,	,,	,,
$C_{12}H_{12}O_4$	220	100·00			

The first and second analyses were made with the products of two different preparations; the third analysis is of the product obtained by treating some of the same substance as served for the second analysis a second time with sodium-amalgam.

Strong sulphuric acid gives a blood-red colour with hydropiperic acid; fuming nitric acid acts in the same way; nitric acid diluted with its own bulk of water acts violently on hydropiperic acid when slightly heated, giving a solution from which water precipitates a semi-fluid nitro-acid. When hydropiperic acid is heated with excess of alkali, a good deal of gas is given off, and the residue exhibits the reactions of the acid $C_7H_6O_4$, obtained by Dr. Matthiessen and myself*, by distilling hemipinic acid with hydriodic acid, and subsequently obtained by Strecker*, by heating piperic acid with excess of potash. With hydriodic acid it behaves in the same way as piperic acid.

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* Proc. Roy. Soc., xi, 58.

Hydropiperate of ammonium, $C_{12}H_{11}(NH_4)O_4$.—This salt was prepared by neutralizing the acid with ammonia. It crystallizes easily from hot water in small shining scales. For analysis, a portion was dissolved in a little water; the acid was precipitated by hydrochloric acid, collected on a weighed filter, and washed with as small a quantity of water as possible; the filtrate was evaporated; the residue dissolved in very little water; the small additional quantity of acid thus separated was collected on the same filter as before, and the whole quantity weighed, after being dried *in vacuo;* the second filtrate and wash-waters were then again evaporated, and the ammonia was determined in the residue as chloro-platinate.

0·4813 grm. salt gave ·4469 grm. hydropiperic acid and ·4126 grm. chloroplatinate of ammonium.

·5147 grm. salt gave ·4787 grm. hydropiperic acid and ·2146 grm. platinum.

	Calculated.		Found.	
$C_{12}H_{12}O_4$	220	92·83	92·85	93·01
H_3N	17	7·17	6·55	7·16
$C_{12}H_{12}O_4H_3N$	237	100·00	99·40	100·17

A strong solution of hydropiperate of ammonium can dissolve a considerable quantity of hydropiperic acid: the addition of strong aqueous ammonia to such a solution saturated with acid, gives an almost solid mass of hydropiperate of ammonium; by the addition of water, it is decomposed into hydropiperate of ammonium, which dissolves, and hydropiperic acid, which is precipitated.

Hydropiperate of potassium with excess of acid, $C_{12}H_{11}KO_4 + C_{12}H_{12}O_4$.—This salt was obtained by boiling a solution of hydropiperic acid in nearly absolute alcohol with excess of dry carbonate of potassium, filtering the solution while still hot, and allowing it to cool: the salt was thus obtained crystallized in hemispherical clumps of radiating needles. It was analysed after being once recrystallized from alcohol and dried at 100°C.

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* Ann. Ch. Pharm., cviii, 280.

0·316 grm. salt gave ·688 grm. carbonic acid and ·1455 grm. water.
0·261 grm. salt gave ·050 grm. sulphate of potassium.

	Calculated.		Found.	
C_{24}	288	60·25	59·38	„
H_{23}	23	4·81	5·11	„
K	39	8·16	„	8·59
O_8	128	26·78	„	„
$C_{24}H_{23}KO_8$	478	100·00		

The deficiency of carbon and excess of potassium shown by the analysis were, no doubt, caused by the presence of a small quantity of neutral hydropiperate of potassium (calc. carbon 55·81 per cent.; potassium 15·12 per cent.); indeed, the acid salt appears to be decomposed by repeated crystallization from alcohol into hydropiperic acid and the neutral potassium-salt, at least a portion which had been recrystallized three times from alcohol gave, on analysis, 12·63 per cent. potassium. The acid salt is immediately decomposed by water, with precipitation of hydropiperic acid.

Hydropiperate of calcium, $C_{12}H_{11}CaO_4(+H_2O\,?)$.—Obtained by boiling the acid with milk of lime, filtering hot, and separating the excess of lime by carbonic acid; or by precipitating a rather strong solution of hydropiperate of ammonium with chloride of calcium. This salt is partially decomposed by solution in hot water, but may be purified by crystallization from a mixture of about 2 parts water and 1 part alcohol, which deposits it in bunches of fine needle-shaped crystals. It is only slightly soluble in cold water. The crystals effloresce in the air, but do not lose all their water below about 100° C.; they melt together to a sticky mass at 100°, which may be powdered when quite dry, and then does not again become soft on heating. Hydropiperate of calcium, dried at 100°, does not further diminish in weight at 120°.[*]

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[*] Hydropiperate of calcium appears to crystallize with one atom of water. A calcium-determination in the air-dry salt gave 7·83 per cent. calcium (the formula $C_{12}H_{11}CaO_4 + H_2O$ requires 7·78 per cent. calcium); after the same salt had stood two days longer over sulphuric acid, it contained 4·2 per cent. water; in other preparations of the salt (air-dry), I found 4·94, 4·88, and 4·87 per cent. water; numbers which do not agree with any simple atomic proportion. The percentage of water calculated for the above formula is 7·00: I can only explain the results obtained, by ascribing them to the rapidity with which the salt effloresces. After drying very quickly, by pressure between paper and exposure to the air, the crystals were found to have partially effloresced when examined under the microscope.

0·595 grm. salt (dried at 105°) gave ·170 grm. sulphate of calcium.

·3348 grm. salt (dried at 100°) gave ·095 grm. sulphate of calcium.

	Calculated.		Found.	
C_{12}	144	60·25	”	”
H_{11}	11	4·60	”	”
Ca	20	8·37	8·30	8·35
O_4	64	26·78	”	”
$C_{12}H_{11}CaO_4$	239	100·00		

Hydropiperate of barium, $C_{12}H_{11}BaO_4$, resembles the calcium-salt, and may be obtained in a similar way. (Found, 23·2 per cent. barium; calculated, 23·8 per cent.)

Hydropiperate of silver, $C_{12}H_{11}AgO_4$.—A crystalline precipitate almost insoluble in cold water; it dissolves in hot water, but is partially decomposed at the same time. It can hardly be dried without undergoing slight decomposition.

0·2933 grm. gave ·0985 grm. metallic silver.

	Calculated.	Found.
Silver per cent. . .	33·03	33·58

A solution of hydropiperate of ammonium gives a whitish brown precipitate with *perchloride of iron,* and white precipitates with *corrosive sublimate, mercurous nitrate,* and *acetate of lead,* all of them soluble in hot water.

Hydropiperate of ethyl.—A solution of hydropiperic acid in absolute alcohol was saturated with hydrochloric acid gas, and heated to 130° for four or five hours; the product was then evaporated on a water-bath, and the residue washed with dilute potash. In this way a neutral brown liquid was obtained, which was heavier than, and insoluble in, water. By solution in ether, treatment of the ethereal solution with animal charcoal, and subsequent evaporation, it was obtained as a brownish yellow liquid. It was not altered by dilute potash or ammonia, but gave a half-solid mass, probably *hydropiperamide,* when saturated with gaseous ammonia.

Hydropiperic acid, heated with an excess of monohydrated acetic acid to 160° C. during 30 hours, appears to be unaltered. The product of this experiment was poured into water, which caused a precipitate of a solid acid; this precipitate was washed to remove acetic acid; about two-thirds of it were then neutralized by lime, the other third added, and the whole evaporated to dryness on a water-bath. The residue was well washed with strong alcohol, the remaining salt crystallized from very dilute alcohol, and then decomposed by hydrochloric acid. The acid thus separated was dried over sulphuric acid, and analysed.

0·3394 grm. acid gave ·810 grm. carbonic acid and ·1724 grm. water. These numbers show that the substance was nearly pure hydropiperic acid, of which it had all the external properties.

	Found.	Hydropiperic acid.
Carbon . . .	65·12	65·46
Hydrogen . . .	5·64	5·45

The deficiency of carbon may, perhaps, indicate that a small quantity of aceto-hydropiperic acid, $C_{12}H_{11}(C_2H_3O)O_4$, (carbon 64·12 per cent.), had been formed.

Hydropiperic acid, heated to 150° C. with chloride of acetyl, gives a neutral oil, insoluble in water and dilute alkalis; probably aceto-hydropiperic anhydride; I do not know whether aceto-hydropiperic acid was formed at the same time or not.

V.—*On the Camphor of Peppermint.*

By A. Oppenheim, Ph.D.

The camphor of peppermint, known as constituting the stearoptene of the essential oil of *Mentha piperita*, has lately been obtained in larger quantities, so as to allow of a closer examination being instituted than has hitherto been possible. It arrives from Japan in coarse earthenware jars, merely protected by paper covers, and consists of a mass of small, white, fragrant, prismatic crystals, resembling sulphate of magnesia, which salt, in fact, seems to be constantly used for the purpose of adulterating the Japanese peppermint-camphor, as from ten to twenty per cent. of that salt may be separated from the camphor by washing it with water. When washed with warm water, the peppermint-camphor melts, and, on congealing, forms itself into a hard crystalline mass. It melts at 36 C, and distils, without decomposition, at 210°. These properties very nearly coincide with those established by Dumas,* for the stereoptene of American oil of peppermint. The composition of these two substances is exactly the same, viz.:

0·260 grm. of Japanese camphor of peppermint, dried at 100°, gave 0·732 grm. of carbonic acid, and 0·315 grm. of water, or in 100 parts.

	Japan camphor of peppermint.	Dumas American camphor.	Calculated.
C	76·93	76·5	76·92
H	13·40	13·1	12·82
O	,,	,,	10·26

This corresponds with the formula established by Dumas, $C_{10}H_{20}O$.† Walter verified this formula in 1830, by determining the vapour-density of the corresponding hydrocarbon, $C_{10}H_{18}$.

The nature of this body which, on many grounds, claims our attention, has not been determined by either of these chemists. Whether it be an alcohol, an aldehyde, a ketone, or of a nature less distinct (like the hydrates of oil of turpentine), it possesses particular interest, from the fact of its bordering on the two great groups of organic chemistry, the group of fatty and that of aromatic bodies. To the former it is related by being isomeric with capric aldehyde, and to the latter, by differing from a number of aromatic bodies, merely in the number of its hydrogen-equivalents.

The camphol of Berthelot, $C_{10}H_{18}O$, differs from it by two equivalents of hydrogen; common camphor, $C_{10}H_{16}O$, by four; the cuminic alcohol of Rossi, $C_{10}H_{14}O$, also thymol and carvacrol, by six; and cuminol, $C_{10}H_{12}O$, by eight equivalents of hydrogen.

The relation of camphol and camphor being that of an alcohol and its aldehyde,‡ the position which the camphor of peppermint holds towards them, will call for our particular attention from their being related, not only as regards their composition, but also with respect to their physical properties. The peppermint-camphor turns the plane of polarization to the left.

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* Gerhardt, Traité de Chimie Organique, vol. iv. p. 357.

† $C = 12$; $H = 1$; $O = 16$.

‡ Berthelot, "La Chimie Organique fondue sur la Synthèse."

A preliminary determination of its rotatory power has been arrived at by the aid of Dubosc's saccharometer. A tube 22mm. in length was filled with a 10 per cent. solution of peppermint-camphor in alcohol, when it was found to deflect the plane of polarization as much as a plate of quartz 0·44mm. thick. This corresponds to an angle of $10{\cdot}56^\circ = a$, and to a molecular rotatory power,—

$$[a] = \frac{a}{l\epsilon\delta} = 59{\cdot}6.$$

Peppermint-camphor is but slightly soluble in water, although it imparts to the liquid a strong odour and taste. It is very soluble in alcohol, ether, sulphide of carbon, and in fatty and essential oils; insoluble in aqueous solutions of alkalies. From an alcoholic solution of soda, it crystallizes in long needles. A current of sulphurous acid or of hydrochloric acid gas dissolves it. By evaporation, the acids pass off, leaving the peppermint-camphor unaltered. Concentrated acids, especially nitric, sulphuric, hydrochloric, formic, acetic, and butyric acid, dissolve it very freely. From these solutions it is separated by water as well as by alkalies, as an oil which soon solidifies and then exhibits the original properties of the camphor.

When concentrated acetic acid is heated with peppermint-camphor in a sealed tube, for ten or twelve hours, at about 120° C., these two bodies combine into a light oil, no longer decomposible by water or by cold solutions of alkalies. After washing with carbonate of soda, and drying over chloride of calcium, it boils between 222° and 224° C. without decomposition.

I. 0·308 grm. of this distillate yielded, by analysis, 0·314 grm. of water and 0·827 grm. of carbonic acid.

The same body is obtained by the action of anhydrous acetic acid on peppermint-camphor.

II. 0·310 grm. thus prepared, gave 0·303 grm. of water and grm. of carbonic acid.

	I.	II.	Calculated.
C	73·06	72·58	72·73
H	11·04	11·18	11·11

This agrees with the formula,—

$$\left.\begin{matrix}C_{10}H_{19}\\ C_2H_3O\end{matrix}\right\} O.$$

That is, peppermint-camphor in which one equivalent of hydrogen has been substituted by acetyl, so as to form a compound ether.

This body is highly refractive, and deflects the plane of polarization to the left more strongly than the camphor from which it is derived. By preliminary observation with the saccharometer, its molecular rotatory power $[\alpha]$ has been found $= 114°$. Hydrate of baryta does not seem to decompose it; but, by heating it with an alcoholic solution of soda, to 120° C. for three hours, it is perfectly decomposed into acetate of soda, and an oil which soon congeals into a crystalline mass, not unlike common camphor. After being pressed between blotting-paper, it distils at 210° C., fuses at 34°, and exhibits otherwise the original properties of peppermint-camphor.

Butyric acid combines with peppermint-camphor on being heated with it to 200° C. for about thirty hours.

The product was separated into two parts, distilling from 230° to 240°, and from 240 to 250° respectively. The former of these portions gave the following analytical results:—

0·287 grm. of the liquid gave 0·303 grm. water, and 0·792 grm. of carbonic acid, corresponding to the formula,

$$\left.\begin{matrix} C_{10}H_{19} \\ C_4H_7O \end{matrix}\right\} O,$$

which is that of butyrate of menthyl; in 100 parts,—

	Found.	Calculated.
C	74·84	74·33
H	11·74	11·50

A preliminary determination of its rotatory power gave $[\alpha] = 88·80°$.

A concentrated solution of hydrochloric acid acts on peppermint-camphor at 100° C. But it is necessary to heat them together for a week in order to obtain a considerable quantity of chloride of menthyl. At a temperature of 120° C., twenty-four hours suffice to complete this reaction.

The chloride of menthyl may be washed with carbonate of soda, but it does not bear distillation. The following analyses were made with non-distilled portions of the liquid dried over chloride of calcium:—

I. 0·323 grm. gave 0·332 grm. of water and 0·794 grm. of carbonic acid.

II. 0·382 grm. gave 0·296 of chloride of silver.

III. 0·310 grm. gave 0·206 grm. of chloride of silver.

This corresponds to the formula $C_{10}H_{19}Cl$, or, in 100 parts,

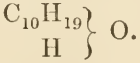
	I.	II.	III.	Calculated.
C	67·06	„	„	68·62
H	11·32	„	„	10·89
Cl	„	19·16	19·67	20·34

The same body was obtained by Walter, by the action of perchloride of phosphorus on peppermint-camphor.

Iodide and bromide of phosphorus react very strongly on this body; but, as the resulting bodies bear distillation as little as the chloride of menthyl, these methods are not advisable for obtaining them. Hydriodic acid combines with peppermint-camphor at about 120° C.

Sodium acts very strongly on peppermint-camphor. It dissolves therein when fused, and disengages hydrogen. By raising the temperature, about one equivalent of sodium may be made to unite with the fused camphor, forming a vitreous, transparent mass, white originally, but becoming brown and moist when exposed to the air. It is decomposed by water, but soluble in absolute alcohol and in iodide of ethyl. The reaction of this body on the sodium-compound is not so simple as might be expected. When heated to 100°, the transparent liquid solidifies, but continues to be soluble in a mixture of ether and alcohol. From this solution, deliquescent crystals may be obtained, which contain iodine, sodium, carbon, and hydrogen; but continued evaporation decomposes these crystals into iodide of sodium and an oily substance, which does not appear to be the mixed ether expected to be formed by such reaction. The products of this and of similar reactions form the subject of the continuation of these researches.

From the compound ethers and the sodium-compound hitherto obtained, it is already evident that the camphor of peppermint is a monatomic alcohol having the formula—



$$\left.\begin{matrix} C_{10}H_{19} \\ H \end{matrix}\right\} O.$$

It belongs to the general type $C_nH_{2n}O$, and is, therefore, homologous with the allylic alcohol of Hofman and Cahours, and with the acetylic alcohol of Berthelot. As it is isologous with campholic alcohol, the name *mentholic alcohol,* or *menthol,* may perhaps be advantageously substituted for that of camphor of peppermint.

The corresponding hydrocarbon, menthene, $C_{10}H_{18}$, which Walter obtained by the action of phosphoric acid, may likewise be produced in various other ways. It has been found among the products of the reaction of chloride of menthyl on ethylate of sodium. The most advantageous way of preparing it seems to be to react on menthol with chloride of zinc. Prepared in this way, the menthene has no action on polarized light. It boils at 163° C.

0·227 grm. yielded, by analysis, 0·282 grm. of water, and 0·733 grm. carbonic acid; in 100 parts—

	Found.	Calculated.
C	86·59	86·94
H	13·65	13·05

Bromine does not combine directly with this hydrocarbon. It reacts on it very violently, disengaging currents of hydrobromic acid, and forming various products of substitution, of no stability whatever, even at ordinary temperatures.

By adding, drop by drop, two equivalents of bromine to one of menthene, monobrominated menthene $C_{10}H_{17}Br$ must be formed, which, by the action of oxide of silver, or of hydrate of soda, might be transformed into camphol. But this reaction gives rise to a hydrocarbon $C_{10}H_{16}$, boiling between 170° and 175° C.

$$C_{10}H_{17}Br + \left.\begin{matrix}K\\H\end{matrix}\right\}O = KBr + \left.\begin{matrix}H\\H\end{matrix}\right\}O + C_{10}H_{16}.$$

The acid corresponding to menthol is identical or isomeric with the campholic acid of Delalande, $C_{10}H_{18}O_2$.

The ordinary oxidizing agents, such as nitric acid, chromic acid, &c., do not produce this acid. They at once attack the carbon of the mentholic alcohol. I hope, however, to be able to produce it by a less direct method of oxidation.

VI.—*On some Physical Properties of the Alloys of Tin and Lead.*

By PROFESSOR BOLLEY.

At the Conference of the Chemico-Technical Section of the Swiss Polytechnic School, at the end of the session 1858-9, the following prize problem was offered for solution, the award to be made in May, 1861:—

1. A survey of all researches hitherto published on the physical properties—especially the hardness, fusibility, and specific gravity, of the alloys of tin and lead.

2. Preparation of *nine* alloys containing definite equivalent quantities of these elements, viz.:—

1 equivalent of tin to $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, 1, $1\frac{1}{2}$, 2, 3, and 4 eq. lead.

3. Determination of the specific gravities and melting points of these alloys; also of their relations as elements of a simple voltaic circuit, in connection with tin, lead, and zinc, and in presence of acids, alkaline liquids, and dilute saline solutions.

The prize was awarded to G. Pillichody, of Bern, from whose Essay we here extract the most interesting results. The experiments were made in the Technological Laboratory of the Institute.

a. Specific Gravity.—From a comparison of the researches of Kupffer, Long, and Thompson, it appears that the specific gravities of the alloys of tin and lead exhibit considerable variation. The author's determinations agree most nearly with those of Long. He found, in accordance with Kupffer, that the specific gravities of these alloys, as determined by experiment, are smaller than the mean values calculated from the quantities and specific gravities of the component metals; but that (contrary to Kupffer's statements) the *expansion*—that is to say, the difference between the observed and calculated densities—is greatest in the alloy SnPb, so that, with an increase in the proportion of either metal, the specific gravities, as determined by experiment and by calculation, approach more nearly to each other.

These relations are exhibited in the following table :—

Specific Gravities of Alloys of Tin and Lead.

	Kupffer.			Long.			Thomson.			Pillichody.			Reg-nault.
	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	
$Sn_4\,Pb$ ...	8,1730	8,1826	96	8,188	8,555	367	7,850	8,545	695	8,2347	8,5507	3160	—
$Sn_3\,Pb$ ...	8,3914	8,3983	69	—	—	—	8,549	9,002	453	8,4087	8,8118	4031	—
$Sn_2\,Pb$ ...	8,7454	8,7518	64	8,779	9,221	442	8,688	9,209	521	8,7257	9,1954	4697	—
$Sn_3\,Pb_2$ ...	—	—	—	—	—	—	—	—	—	9,0377	9,5054	4677	9,387
$Sn\,Pb$	9,4263	9,4366	103	9,460	9,912	452	9,288	9,899	611	9,4330	9,9052	4772	—
$Sn_2\,Pb_3$ ...	—	—	—	—	—	—	—	—	—	9,7971	10,2603	4632	—
$Sn\,Pb_2$ ...	10,0782	10,3936	154	10,080	10,480	404	—	—	—	10,0520	10,4763	4243	—
$Sn\,Pb_3$ ...	10,3862	10,4122	260	—	—	—	—	—	—	10,3311	10,7296	3985	—
$Sn\,Pb_4$ ...	10,5551	10,6022	451	10,590	10,875	285	—	—	—	10,5957	10,8686	2729	—

The author's results afford an additional proof that very little dependence is to be placed on the hydrostatic method for the determination of the composition of lead and tin alloys.

b. Melting points.—The statements of different authors respecting the melting points of the alloys of tin and lead, exhibit even greater discordance than those which relate to the specific gravities. Most of those who occupied themselves with the subject prior to the investigations of Rudberg, or without knowledge of those investigations, neglected to observe a very important circumstance, perhaps the most interesting of all, connected with it. This circumstance is easily overlooked, if only the *melting* point be observed, instead of the solidifying point, which gives much more trustworthy results. When the latter method is followed, the thermometer immersed in the melted alloy usually exhibits, during the passage of the mass from the liquid to the solid state, two stationary points. This effect is due to the separation of one or other of the component metals, while an alloy of constant composition still remains liquid. This alloy has the composition Sn_3Pb. An alloy richer in lead would first deposit lead, and an alloy, containing a larger proportion of tin, would first deposit tin—the alloy Sn_3Pb. remaining liquid for a longer or shorter time, and ultimately solidifying at about 181° C. This temperature, therefore, corresponds to the lowest melting point that can be exhibited by an alloy of tin and lead, a larger proportion of either metal causes the melting point to rise.

Rudberg determined only the intervals of time which elapsed during the fall of temperature through each 10°C. He also employed a thermometer, the zero of which, according to his own statement, had not been exactly determined. Pillichody's experiments, on the other hand, were made with an exact thermometer, and with all the precautions required in observations of this kind. In all these determinations, the constant solidifying point was found to be exactly 181°C.

Table of the Melting Points of Alloys of Tin and Lead.

	Pillichody.	Rudberg.	Thomson.	Kupffer.	Parkes, for
$Sn_4 Pb$	187	190 – 180	190	189	(9 Sn + 4 Pb) 173
$Sn_3 Pb$	181	190 – 180	182·8	186	(6 + 4) 168·8
$Sn_2 Pb$	197	210 – 200	182·8	196	(4 + 4) 188·8
$Sn_3 Pb_2$	210	—	—	—	—
$Sn Pb$	235	250 – 240	182·2	241	(4 + 7) 215·7
$Sn_2 Pb_3$	246	—	—	—	(4 + 10) 243·3
$Sn Pb_2$	270	280 – 290	—	289	(4 + 14) 254·4
$Sn Pb_3$	283	290 – 280	—	—	(4 + 22) 269·4
$Sn Pb_4$	292	—	—	—	(4 + 28) 275

This Table shows that Thomson, who probably also sought for the solidifying point, overlooked the *variable*, and observed the thermometer in the neighbourhood of the *constant* solidifying temperature. Of this constant point, no notice is taken either by Parkes or by Kupffer.

VII.—*New experiments on the Dangers arising from the use of Certain Waters for feeding Steam Boilers.*

By Professor Bolley.

It has hitherto been received, as a kind of dogma in chemico-technical literature, that waters which, when evaporated, deposit only the *carbonates* of lime and magnesia, are better adapted for feeding steam-boilers than those which likewise yield *sulphate of lime,* because the latter salt, even in small quantity, imparts to the deposit a stony coherence, whereas the carbonates are deposited in the form of a soft mud. That serious mischief may arise from the formation of a stony incrustation on the surface of a boiler is well known, whereas the deposition of merely pulverulent matter has not hitherto been observed to create much inconvenience. Most of the remedies proposed for these evils have likewise for their object the conversion of the sulphate of lime into carbonate; that is to say; the production of a muddy in place of a stony deposit; such for example is the action of carbonate of soda.

Since the practice of heating steam boilers with coal has been introduced into Switzerland, many serious disturbances have been observed in the functions of boilers which were quite unknown so long as they were heated with wood. Both old and new boilers heated from within (the Cornish or Fairbairn construction) have become red-hot at the upper part of the flue near the fire-place, while the water-gauge showed that the level of the water was several inches above the heating surface. The boiler-plates started, and had to be taken out and replaced by new ones, but without any diminution of the evil.

The first of these cases, in which, as well as in the second, I was consulted by the well-known engineering firm of Escher, Wyss, and Co., happened in the Canton Zurich. The water used for feeding the boiler was taken from the Jenabach, on the southern declivity of the Bachtel. Samples from different parts of the stream were sent to me for examination. Three samples were analysed, and yielded the following proportions of solid matter and carbonate of lime :

In 1 litre.		Total solid residue.	Carbonate of lime.
Sample *a.*	..	0·272 grm.	0·2226 grm.
„ *b.*	..	0·2324 „	
„ *c.*	..	0·2426 „	0·2010 „

The water contained very little organic matter; *sulphates were entirely absent;* silica alumma, magnesia, and alkaline salts were present in small quantity only, as compared with the carbonate of lime. The water may be described as pure, but rather hard—the hardness being of the kind called temporary.

It was suggested that the mischief above mentioned might arise from the circumstance that, above the place at which the water was drawn for feeding the boiler, the refuse water of a bleach-work was discharged into the stream. A bottle of the waste bleaching liquid was, therefore, likewise sent for examination. It contained, in solution, quick lime, chloride of calcium, and a small quantity of decomposed chloride of lime. On mixing it with the water of the stream, a strongly milky turbidity was produced. So far there was nothing that might not have been expected: but at the top of the liquid in the bottle there was a layer of *fatty matter;* which, after mixing with water, solution in ether, and evaporation, remained in the form of a thickish oil. How this comparatively large quantity of fatty matter got into the bleaching liquid could not be ascertained.

The boiler contained a considerable quantity of a whitish *grey pulverulent deposit*, consisting essentially of carbonate of lime. By careful searching, however, certain substances were found in it mechanically mixed; viz.: black scaly particles of iron, ferric oxide, and adhering organic matter, which became perceptible on heating, and red granules, which were found to consist of the remains of a red lead cement. The powder separated from the water exhibited a further peculiarity. When thrown on water, *it swam on the surface, did not become wet, but remained in its place, and dry, even after prolonged boiling.*

A portion of this powder was well dried on the water bath, and then treated with ether, which extracted a small quantity of fatty matter.

The cause of the phenomenon above-mentioned was now apparent. The pulverulent deposit in the boiler completely covered the heated surface of the flue, so that this surface did not come in contact with the water. The quantity of powder in the boiler was so large that it must have formed a layer several inches thick.

The fatty substance which had found its way into the water surrounded the particles of the precipitated carbonate of lime with a layer *which could not be wetted by the water;* and, in consequence of this want of adhesion, the powder was kept floating on the surface. The powder, after being treated with ether and dried, sank easily under water, and in its original state was easily wetted by alcohol.

The preceding investigations did not, however, afford any precise information as to the nature of the fatty substance. But shortly afterwards, I was made acquainted with another accident of exactly the same kind, which happened to a boiler in the Canton Thurgau. The water with which this boiler was supplied was found to contain, as a means of two experiments, 0·2417 grm. solid matter per litre, 0.045 of which consisted of organic matter, containing traces of nitrogen. The residue from four or five litres of this water was distilled with a slight excess of dilute sulphuric acid: the distillate had a distinct odour of butyric acid.

In this boiler also a considerable quantity of whitish pulverulent matter was deposited, which, so far as I could ascertain, was free from mechanical impurities. This powder also was *not wetted by water*.

On boiling half a pound of it with distilled water, and gradually adding *carbonate of soda*, the powder was at length thrown dowr to the bottom, and an alkaline liquid was formed, containing the fatty substance in solution. After filtration and concentration, it was mixed with a small quantity of hydrochloric acid; the odour of butyric acid then became perceptible, and small drops of fat were separated, which did not disappear on dilution with water, but, by agitation with ether, and subsequent evaporation, yielded a small quantity of a nearly odourless oily body.

I was, at first, of opinion that the butyric acid might have existed naturally in the water, inasmuch as this acid has been found in many waters derived from peat-bogs; but, on discovering the fat insoluble in water, I abandoned this view, and subsequently learnt from Mr. Jackson, Director of the factory of Escher, Wyss, and Co., that the water supplied to the boiler was taken from the condenser of another steam-engine, and consequently might have derived the fat from that source. It showed, however, scarcely any turbidity; and all the results obtained with it led to the conclusion that the quantity of fat contained in it was very small. Practically, the origin of the fatty matter is of little consequence.

By my recommendation, a small quantity of solution of carbonate of soda was added to the water supplied to the boiler, and by this means the inconvenience above described was completely obviated. It likewise ceased when the water was no longer taken from the condenser of the other engine.

I regard these experiments as well worthy of attention. That observations of such cases, and enquiries into their causes, have been previously published, I have not been able to find. Nevertheless, though various conditions must conspire to produce the result in question, it is very probable that such concurrence frequently takes place.

The results of this investigation may be summed up as follows :—

1. When a boiler is fed with water which deposits only carbonates unmixed with sulphates, the presence of very small quantities of fatty matter may cause the deposit to assume a dusty instead of a muddy consistence. Under such circumstances, rubbing the inside of the boiler with grease can only do mischief.

2. This pulverulent character of the deposit may cause those portions of the boiler-surface which are strongly heated and directly covered by the powder to become red-hot, thereby giving rise to explosions and all their attendant consequences.

3. In such cases, as well as when the water contains sulphates, the addition of a small quantity of carbonate of soda will be found very useful.

4. The effect, so far as regards the form of the deposit, is probably independent of the kind of fuel employed : it appears, however, from the observations hitherto made, that the heating of the boiler plates to redness takes place only when the fires are fed with coal, this kind of fuel producing a more intense heat in the immediate neighbourhood of the burning mass.

VIII.—*On the Construction of Tables exhibiting the Composition and Mutual Relations of Organic Substances.*

By John A. R. Newlands, F.C.S.

These Tables may be formed by arranging all homologous series (whether known or otherwise) in two directions, vertically, according to the difference in the number of equivalents of C and H, and horizontally, according to the number of equivalents of O, contained in the general formula of each series, or *vice versâ*.

The accompanying Table may serve as a specimen of those of a more complete character: it is divided into a number of types, under each of which are placed all substances homologous, or isomeric, with each other.

The following are the principal relations observed on contrasting bodies belonging to these various types:—

I. *Vertically.*

1. Bodies differing by H_2: as $C_5H_{12}O_2''$ amyl-glycol; $C_5H_{10}O_2$ valerianic acid; $C_5H_8O_2$ angelic acid; and $C_5H_6O_2$ picrotoxin.
2. Bodies differing by C: as $C_2H_6O''_2$ ethyl-glycol; $C_3H_6O_2$ propylic acid; $C_4H_6O_2$ crotonic acid; $C_5H_6O_2$ picrotoxin; $C_6H_6O_2$ oxyphenic acid; $C_7H_6O_2$ benzoic acid; and $C_9H_6O_2$ cumarin.
3. Bodies in which C and H_2 replace each other: as $C_4H_8O_2$ butyric acid; $C_5H_6O_2$ picrotoxin; and $C_6H_4O_2$ kinone.
4. Bodies in which C and H_4 replace each other: as butyl-glycol $C_4H_{10}O_2''$; and picrotoxin $C_5H_6O_2$.
5. Bodies differing by CH_4: as $C_7H_6O_2$ benzoic acid; $C_8H_{10}O_2$ terebentilic acid; $C_{10}H_{18}O_2$ campholic acid; and $C_{11}H_{22}O_2$ margaritic acid.

II. *Horizontally.* Bodies differing by O: as C_3H_6'' propylene, C_3H_6O propyl-aldehyde, or allylic-alcohol; $C_3H_6O_2$ propylic acid; $C_3H_6O_3$ lactic acid; and $C_3H_6O_4$ glyceric acid.

III. *Diagonally, from left to right.*

1. Bodies in which O and H_2 replace each other: as C_2H_6O alcohol; $C_2H_4O_2$ acetic acid; and $C_2H_2O_3$ glyoxylic acid.
2. Bodies differing by CO: as CH_4O methylic alcohol, $C_2H_4O_2$ acetic acid; C_3H_4O pyruvic acid; $C_4H_4O_4''$ fumaric acid; and $C_7H_4O_7'''$ meconic acid.

*3. Bodies differing by CO_2. A few of these are here given, from which it may be seen that monobasic, bibasic, and tribasic acids, and also hydrocarbons and alcohols, may be formed from each other by the addition or subtraction of CO_2.

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* The diagonal line exhibiting this relation is drawn from the space immediately to the right of a substance; and, in the case marked thus †, from the space immediately to the left. In the remaining instances, the diagonal lines are drawn directly from the substance itself.

Hydrocarbons, alcohols, &c.	Monobasic acids.	Bibasic acids.	Tribasic acids.
H_2 hydride of hydrogen CH_4 ,, methyl C_2H_6 ,, ethyl	CH_2O_2 formic acid $C_2H_4O_2$ acetic acid $C_3H_6O_2$ propylic acid	$C_2H_2O_4''$ oxalic acid $C_3H_4O_4''$ $C_4H_6O_4''$ succinic acid	$C_3H_2O_6'''$ $C_4H_4O_6'''$ $C_5H_6O_6'''$
$C_2H_6O_2$ ethyl-glycol	$C_3H_6O_4$ glyceric acid	$C_4H_6O_6''$ tartaric acid	$C_5H_6O_8'''$
CH_4O methylic alcohol C_2H_6O ethylic ,, C_3H_8O propylic ,,	$C_2H_4O_3$ glycolic acid $C_3H_6O_3$ lactic acid $C_4H_8O_3$	$C_3H_4O_5$ tartronic acid $C_4H_6O_5''$ malic acid $C_5H_8O_5''$	$C_4H_4O_7'''$ $C_5H_6O_7'''$ $C_6H_8O_7'''$ citric acid
$C_8H_{10}O_2$	$C_9H_{10}O_4$ everninic acid	$C_{10}H_{10}O_6''$ hemipinic acid	$C_{11}H_{10}O_8'''$
C_2H_4'' ethylene C_3H_6'' propylene	$C_3H_4O_2$ acrylic acid $C_4H_6O_2$ crotonic acid	$C_4H_4O_4''$ fumaric acid $C_5H_6O_4''$ citraconic acid	$C_5H_4O_6'''$ [acid $C_6H_6O_6'''$ aconitic
C_6H_6 benzol C_7H_8 toluol	$C_7H_6O_2$ benzoic acid $C_8H_8O_2$ toluylic acid	$C_8H_6O_4''$ phthalic acid $C_9H_8O_4''$ insolinic acid	$C_9H_6O_6'''$ $C_{10}H_8O_6'''$
C_4H_4O C_5H_6O	[acid $C_5H_4O_3$ pyrocomenic $C_6H_6O_3$ pyrogallic acid	$C_6H_4O_5''$ comenic acid $C_7H_6O_5''$ gallic acid	[acid $C_7H_4O_7'''$ meconic $C_8H_6O_7'''$

IV. *Diagonally, from right to left.*

1. Bodies differing by H_2O: as $C_6H_{10}O_8''$ mucic acid; $C_6H_8O_7'''$ citric acid; $C_6H_6O_6'''$ aconitic acid; and $C_6H_4O_5''$ comenic acid.
2. Bodies in which C and O replace each other: as $C_3H_4O_5$ tartronic acid; $C_4H_4O_4''$ fumaric acid; $C_5H_4O_3$ pyrocomenic acid; and $C_6H_4O_2$ kinone.

†3. Bodies in which C and O_2 replace each other: as $C_4H_6O_6''$ tartaric acid; $C_5H_6O''_4$ citraconic acid; and $C_6H_6O_2$ oxyphenic acid.

A table of this sort constitutes, as it were, a map of Organic Chemistry, wherein each substance is surrounded by its derivatives, and those from which it is derivable. Thus, relations between the formulæ of bodies cannot fail to be detected by the most casual observer, many of which might otherwise escape the view of those well acquainted with the science. For instance, the formula of kinic acid $C_7H_{12}O_6''$ is homologous with that of tartaric acid $C_4H_6O_6''$,—a relation which is confirmed by the similarity of their crystals. This suggests the possibility of pimelic acid $C_7H_{12}O_4''$ being formed by the reduction of kinic acid, just as succinic acid $C_4H_6O''_4$ is formed from tartaric, or *vice versâ*. An unknown homologue of malic acid $C_4H_6O_5''$, having the composition $C_7H_{12}O_5''$, might also be produced, and would serve as a connecting link between pimelic and kinic acids.

Other homologous formulæ are,—

elanic acid......$C_{10}H_8O_5$	Orsellinic acid ...$C_8H_8O_4$	Alpha-orsellic acid $C_{16}H_{14}O_7$	Parellic acid............$C_9H_6O_4$
elasinic acid $C_{12}H_{12}O_5$	Everninic acid $C_9H_{10}O_4$	Evernic acid.........$C_{17}H_{16}O_7$	Hydropiperic acid $C_{12}H_{12}O_4$

&c., &c.

The principal substitution-product of each substance might be placed beneath it.

Compounds containing nitrogen may be placed in the same Table with non-nitrogenous bodies, by first giving the substances containing C, H, and O only, and afterwards, immediately below, those containing these elements with the addition of one or more atoms of N, P, &c. Or separate tables may be formed of bodies containing carbon, hydrogen, and nitrogen, with their various stages of oxidation. In these, the substances would differ diagonally by CN, NH_3, and the oxides of N.

The mode of classification employed in these Tables has been more or less dilated upon by Messrs. Foster, Schiel, and other chemists; but as I have had them by me now for some years, and none have hitherto been published, I am induced to offer them to the notice of chemists, as a means of suggesting hundreds of reactions, and of showing not only what has been already achieved, but likewise what remains to be accomplished by future researches.

Extract from a Table, exhibiting the Composition and Mutual Relations of Organic Substances. By John A. R. Newlands, F.C.S.

C_nH_{2n+2} CH_4 hydride methyl C_2H_6 hydride ethyl C_3H_8 hydride propyl	$C_nH_{2n+2}O$ CH_4O methylic alcohol C_2H_6O ethylic alcohol C_3H_8O propylic alcohol	$C_nH_{2n+2}O_2$ CH_4O_2'' $C_2H_6O_2''$ ethyl-glycol $C_3H_8O_2''$ propyl-glycol	$C_nH_{2n+2}O_3$ CH_4O_3''' $C_2H_6O_3'''$ $C_3H_8O_3'''$ glycerin	$C_nH_{2n+2}O_4$ CH_4O_4 $C_2H_6O_4$ $C_3H_8O_4$	$C_nH_{2n+2}O_5$ CH_4O_5 $C_2H_6O_5$ $C_3H_8O_5$	$C_nH_{2n+2}O_6$ CH_4O_6 $C_2H_6O_6$ $C_3H_8O_6$
C_nH_{2n} CH_2'' methylene C_2H_4'' ethylene C_3H_6'' propylene	$C_nH_{2n}O$ CH_2O C_2H_4O aldehyde C_3H_6O allylic alcohol	$C_nH_{2n}O_2$ CH_2O_2 formic acid $C_2H_4O_2$ acetic ,, $C_3H_6O_2$ propylic ,,	$C_nH_{2n}O_3$ CH_2O_3'' carbonic acid $C_2H_4O_3$ glycolic ,, $C_3H_6O_3$ lactic ,,	$C_nH_{2n}O_4$ CH_2O_4 $C_2H_4O_4$ $C_3H_6O_4$ glyceric acid	$C_nH_{2n}O_5$ CH_2O_5 $C_2H_4O_5$ $C_3H_6O_5$	$C_nH_{2n}O_6$ CH_2O_6 $C_2H_4O_6$ $C_3H_6O_6$
C_nH_{2n-2} C_2H_2 acetylen C_3H_4 C_4H_6	$C_nH_{2n-2}O$ C_2H_2O C_3H_4O C_4H_6O	$C_nH_{2n-2}O_2$ $C_2H_2O_2$ glyoxal $C_3H_4O_2$ acrylic acid $C_4H_6O_2$ crotonic ,,	$C_nH_{2n-2}O_3$ $C_2H_2O_3$ glyoxylic acid $C_3H_4O_3$ pyruvic ,, $C_4H_6O_3$	$C_nH_{2n-2}O_4$ $C_2H_2O_4''$ oxalic acid $C_3H_4O_4$ $C_4H_6O_4''$ succinic ,,	$C_nH_{2n-2}O_5$ $C_2H_2O_5$ [acid $C_3H_4O_5''$ tartronic $C_4H_6O_5''$ malic acid	$C_nH_{2n-2}O_6$ $C_2H_2O_6$ $C_3H_4O_6$ $C_4H_6O_6''$ tartaric acid
C_nH_{2n-4} C_3H_2 C_4H_4 C_5H_6	$C_nH_{2n-4}O$ C_3H_2O C_4H_4O C_5H_6O	$C_nH_{2n-4}O_2$ $C_3H_2O_2$ $C_4H_4O_2$ $C_5H_6O_2$ picrotoxin	$C_nH_{2n-4}O_3$ $C_3H_2O_3$ $C_4H_4O_3$ $C_5H_6O_3$	$C_nH_{2n-4}O_4$ $C_3H_2O_4$ [acid $C_4H_4O_4''$ fumaric $C_5H_6O_4''$ citraconic [acid	$C_nH_{2n-4}O_5$ [acid $C_3H_2O_5''$ mesoxalic $C_4H_4O_5$ $C_5H_6O_5$	$C_nH_{2n-4}O_6$ $C_3H_2O_6$ $C_4H_4O_6$ $C_5H_6O_6$
C_nH_{2n-6} C_4H_2 C_5H_4 C_6H_6 benzol	$C_nH_{2n-6}O$ C_4H_2O C_5H_4O C_6H_6O phenylic alcohol	$C_nH_{2n-6}O_2$ $C_4H_2O_2$ $C_5H_4O_2$ $C_6H_6O_2$ oxyphenic acid	$C_nH_{2n-6}O_3$ $C_4H_2O_3$ [acid $C_5H_4O_3$ pyrocomenic $C_6H_6O_3$ pyrogallic acid	$C_nH_{2n-6}O_4$ $C_4H_2O_4$ mellitic acid $C_5H_4O_4$ $C_6H_6O_4$	$C_nH_{2n-6}O_5$ $C_4H_2O_5$ $C_5H_4O_5$ $C_6H_6O_5$	$C_nH_{2n-6}O_6$ $C_4H_2O_6$ $C_5H_4O_6$ [acid $C_6H_6O_6'''$ aconitic
C_nH_{2n-8} C_5H_2 C_6H_4 chrysen C_7H_6	$C_nH_{2n-8}O$ C_5H_2O C_6H_4O C_7H_6O saliretin	$C_nH_{2n-8}O_2$ $C_5H_2O_2$ $C_6H_4O_2$ kinone $C_7H_6O_2$ benzoic acid	$C_nH_{2n-8}O_3$ $C_5H_2O_3$ $C_6H_4O_3$ $C_7H_6O_3''$ salicylic acid	$C_nH_{2n-8}O_4$ $C_5H_2O_4$ $C_6H_4O_4$ $C_7H_6O_4$	$C_nH_{2n-8}O_5$ $C_5H_2O_5$ croconic acid $C_6H_4O_5''$ comenic ,, $C_7H_6O_5''$ gallic ,,	$C_nH_{2n-8}O_6$ $C_5H_2O_6$ $C_6H_4O_6$ $C_7H_6O_6$
C_nH_{2n-10} C_6H_2 C_7H_4 C_8H_6	$C_nH_{2n-10}O$ C_6H_2O C_7H_4O C_8H_6O	$C_nH_{2n-10}O_2$ $C_6H_2O_2$ $C_7H_4O_2$ $C_8H_6O_2$	$C_nH_{2n-10}O_3$ $C_6H_2O_3$ $C_7H_4O_3$ $C_8H_6O_3$	$C_nH_{2n-10}O_4$ $C_6H_2O_4$ $C_7H_4O_4$ ellagic acid $C_8H_6O_4''$ phthalic ,,	$C_nH_{2n-10}O_5$ $C_6H_2O_5$ $C_7H_4O_5$ $C_8H_6O_5$	$C_nH_{2n-10}O_6$ $C_6H_2O_6$ [acid $C_7H_4O_6'''$ chelidonic $C_8H_6O_6$

IX.—*Note on a Method of effecting the substitution of Chlorine for Hydrogen in Organic Compounds.*

By Hugo Müller.

In the investigation of Burmese naphtha, made a few years ago by Mr. Warren De La Rue and myself, we endeavoured to obtain some definite iodine-compounds of the hydrocarbons contained in it, by acting upon them with mono-and ter-chloride of iodine, hoping that this reagent would act in this case in a similar way to that observed a short time before by Brown, in the case of pyromeconic acid. These experiments did not however give the expected result, but merely the same chlorine-compounds that were already obtained by using chlorine only. The result was the same when iodine was dissolved in the hydro-carbon and chlorine passed into the deep violet-coloured solution. The only difference observable between the action of chlorine in presence of iodine and that of chlorine only, was that, in the former case, the action took place much more quickly than in the latter.

Having some time ago commenced a series of experiments with the view of obtaining from benzole the corresponding alcohol and acid, I had occasion to investigate the action of chlorine on this hydrocarbon.

Chlorine is absorbed to some extent by benzole, but if light be excluded, no perceptible action takes place until the benzole is heated to the boiling point; hydrochloric acid is then liberated and chlorine-derivatives are formed, but very slowly. In this reaction two series of compounds are formed, namely,

$$\begin{array}{lll} C_6H_6Cl_2, & C_6H_6Cl_4, & C_6H_6Cl_6, \text{ and} \\ C_6H_5Cl, & C_6H_4Cl_2, & C_6H_3Cl_3 \end{array}$$

The experience gained in the above-mentioned experiments with Burmese naphtha, induced me to try upon a large scale the action of chlorine upon benzole in the presence of iodine.

When chlorine is passed into a saturated solution of iodine in benzole, it is completely absorbed, even when the current is moderately rapid, and after the violet solution has become brownish red, owing to the formation of monochloride of iodine, hydrochloric acid is liberated and chlorine-derivatives are rapidly formed. In this way, I have obtained the compounds C_6H_5Cl, $C_6H_4Cl_2$, $C_6H_3Cl_3$, and when an excess of chlorine was used, a beautiful crystalline compound, which was previously obtained in small quantities on treating the hydrocarbons of Burmese naphtha in the same manner. It deserves to be noticed, that whereas when chlorine acts alone upon benzole, the chief products of the reaction are formed by its direct union with the hydrocarbon, the action of chlorine in presence of iodine gives rise to substitution-products and the evolution of hydrochloric acid.

I reserve the detailed description of the products of this reaction, and the method of obtaining them in a pure state for a future communication; what I wish especially to draw attention to upon this occasion is the remarkable effect of iodine in facilitating the action of chlorine upon organic compounds. I have already ascertained that many substances which are acted upon with great difficulty by chlorine alone, and some of them only with the aid of direct sunlight, yield chlorine-products with great ease when acted upon, in the manner described, by chlorine in the presence of iodine.

I have found for instance that benzoic acid dissolved, together with some iodine in chloroform, is acted upon by chlorine very readily, with evolution of hydrochloric acid.

Bisulphide of carbon in which iodine is dissolved is acted upon by chlorine very freely at its boiling point, giving chloride of carbon, chloride of sulphur, and a highly volatile substance having a very irritating and pungent odour, which is perhaps the chlorosulphide of carbon which Kolbe believed he had obtained by exposing sulphide of carbon to the action of chlorine in direct sunlight. The process I have described promises to give this substance in sufficient quantity to admit of ascertaining its true nature.

When chlorine is passed into a solution of iodine in glacial acetic acid in the cold, terchloride of iodine is formed, but the acid is not acted upon. If however the acid is kept boiling whilst the chlorine is being passed into it, hydrochloric acid is given off and chloracetic acid is formed, even in the dark. This affords a ready means of obtaining chloracetic acid, a substance whose preparation according to the usual method requires the aid of strong sunlight, and is commonly very tedious. If the action of chlorine be continued, a higher chlorinated acid is obtained, which does not solidify even at 0° C., and which appears to be bi-chloracetic acid.*

It seems likely, that in this reaction, the iodine acts merely as a carrier and condenser of the chlorine; the effect is very similar to that of some perchlorides, like pentachloride of antimony, and in some cases pentachloride of phosphorus, which act upon many organic substances as if they were mixtures of terchlorides with free chlorine.

I may instance here the formation of Dutch liquid from olefiant gas and pentachloride of antimony, according to Wöhler, and the case of the transformation of bisulphide of carbon into chloride of carbon and chloride of sulphur by means of pentachloride of antimony mentioned by Hofmann.

On comparing the action of pentachloride of antimony with that of chlorine, in presence of iodine, upon the substances above mentioned, I find that the former agent is rather more energetic and possesses a tendency to produce the higher chlorinated derivatives.

Benzole added in small quantities to pentachloride of antimony, is acted upon with great violence, and there is at once formed a chlorinated derivative, which crystallises in beautiful white prisms nearly insoluble in alcohol, and not acted upon by alcoholic potash.

Succinic acid, when brought in contact with pentachloride of antimony, soon evolves hydrochloric acid, and if the reaction is supported by application of heat, chlorosuccinic acid is formed. If however the mixture of succinic acid with pentachloride of antimony be kept warm whilst a current of chlorine is passing into it, the succinic acid is gradually decomposed into volatile products.

I am still engaged with the examination of some new products of these reactions, a full account of which I hope shortly to lay before the Society.

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* Since the above was written I have found that, together with the chloracetic acid, there is invariably some iodacetic acid formed, and it appears that the formation of the latter is favoured by an excess of iodine used in the process. I have not ascertained whether the remarkable compounds lately obtained by Schützenberger by the action of chloride of iodine upon acetate and benzoate of sodium are formed when chlorine acts upon acetic and benzoic acid in the presence of iodine; but as these compounds are already decomposed at 100° C. their formation can hardly be expected under the circumstances.

X.—*On the Constitution of Anthracene or Paranaphthalin and some of its Products of Decomposition*

By Thomas Anderson, M.D., F.R.S.E.,
Professor of Chemistry in the University of Glasgow.

[Abstracted from the Transactions of the Royal Society of Edinburgh, vol. xxii, part iii.]

The solid compounds of carbon and hydrogen form a class of substances to which chemists have scarcely, as yet, paid that attention which their importance and interest appear to merit. With the exception of naphthalin, very little is known regarding them, and it is remarkable that the numerous and varied products of decomposition obtained from that singular substance should not have induced a more minute examination of the kindred compounds, whose existence has been indicated by different chemists. The interest attaching to these compounds is all the greater, because, according to their discoverers, several of them are isomeric, or at least polymeric, with naphthalin; and a more careful examination of them might be expected to throw some light on their intimate constitution and their relations to that body.

No fewer than five substances said to be polymeric with naphthalin have been described. These are *paranaphthalin* or *anthracene*, *metanaphthalin* or *retisterene*, *pyrene*, and two substances not yet named, which occur, together with benzene and benzophenone, among the products of the destructive distillation of benzoate of lime, and are apparently quite distinct from one another and the other three. All of these substances, except naphthalin, have hitherto been obtained in small, and some of them in very minute quantity, so that their constitution has been in most instances fixed by analysis alone; and the difficulties attending the analysis of highly carbonaceous compounds at the time they were made, as well as the absence of any control derived from the examination of their products of decomposition, have naturally occasioned some doubts as to the accuracy of the formulæ assigned to them.

Paranaphthalin or anthracene, which was discovered by Dumas and Laurent in the year 1832,* is the only one of these substances whose examination has extended beyond the mere analysis; and the determination of its vapour-density by the former chemist gave for it the formula $C_{30}H_{12}$, which the examination of some of its decomposition-products by the latter was supposed to confirm. A critical examination of Laurent's experiments by no means bears out this opinion. They are in many respects extremely imperfect, were obviously made on a very small quantity of material, and the formulæ (mostly deduced from a single analysis) are so improbable, that there can be but one opinion as to the necessity for submitting the subject to a further investigation.

Anthracene, as is well known from the observations of Dumas and Laurent, is met with only among the latter portions of the distillation of coal-tar. It has been little seen by chemists, because hitherto the distillation has not generally been pushed so far as to yield it in quantity; but during the last few years, the demand for the asphalt and the higher oils having increased, the distillation has been carried further, and it has been found abundantly in some of the products, and even been used in the manufacture of machinery grease. I have availed myself of the opportunity which a large supply afforded, of extending the examination of anthracene, and with the result of showing that its constitution differs from that attributed to it by its discoverers, and that it is not polymeric with naphthalin.

Before entering on the details of my own experiments, it may be advisable to recapitulate shortly the history of the substance. As already stated, it was discovered by Dumas and Laurent, working in concert, in 1832, and described by the former chemist, who attributed to it the formula $C_{30}H_{12}$, with which his results corresponded very closely. In 1835, Laurent† described, under the name of *paranaphthalese*, a compound to which he gives the formula $C_{30}H_8O_4$, and he appears to have regarded it as a direct product of the action of nitric acid on anthracene. In a subsequent paper‡ he extends his investigation in this direction, and describes no fewer than five different nitro-compounds, and assigns to them very problematical formulæ. In this paper, he again refers to paranaphthalese, but under the name of *anthracenuse*, giving it the formula $C_{30}H_7O_5$, and stating that it is not a product of the direct action of nitric acid on anthracene, but formed by the decomposition of a nitro-compound, in a manner precisely similar to that in which naphthase is obtained from nitronaphthalin. He mentions that a substance of similar properties is obtained from several of the nitro-compounds he prepared, but leaves it an open question whether it is in all cases the same, or whether it differs in constitution according to the nitro-compound from which it is produced. He also describes a chlorine substitution-product, and adopts the name of *anthracene*—a change even then advisable, and which the results of my investigation show to be quite indispensable.

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* Ann. Ch. Phys., 1, 187.

† Ann. Ch. Phys., lx. 220.

‡ *Ibid.*, lxxii. 415.

Crude anthracene is in the form of a soft yellow mass, not unlike palm oil, but with a greenish tinge and harder consistence; in this state, it contains a little naphthalin and a considerable quantity of oil of high boiling point, which causes it to leave a greasy stain on paper, and to melt easily when rubbed between the fingers. It has a decided though not strong smell, due partly to the naphthalin, but still more to the oil with which it is contaminated, and which it loses on purification. It is soluble, though not abundantly, in alcohol, but dissolves with tolerable facility in ether, turpentine, and still better in benzole. Methylated spirit was in the first instance used for its purification. The first solution, on cooling, deposited thick oily globules, with a small quantity of crystals; but after several successive quantities of spirit had been used, crystals were deposited free from oil, but still retaining the yellow colour of the original substance, and—apparently, owing to the removal of the oil—were much less soluble in new quantities of spirit. By repeated crystallisations, it was found possible to obtain the anthracene quite colourless; but the process was too tedious to be employed for preparing it on the larger scale. Other solvents, and more particularly benzole, were likewise tried; but, though preferable, the complete removal of the colouring matter is difficult with them also, and it was found necessary to begin by distilling the crude substance in a small iron still. The first portions which passed over during the process contained much naphthalin and oil, but were quite free from colour. As the distillation proceeded, however, the colour gradually increased, and at the end a small quantity of a dark green substance remained in the retort. The first portions of the distillate were pressed to remove the oil, and the last portions redistilled so as to get rid of the colour as completely as possible, and the purification finished by repeated crystallisation from benzole, and sometimes by sublimation.

Anthracene is deposited from its solution in perfectly colourless scales, generally of very small size, even when large solutions have been allowed to cool. Those obtained from spirit are generally the best, and when suspended in the solution, have a fine satiny lustre, which they lose to some extent when dried. From benzole the crystals are somewhat granular, and less brilliant in appearance. By sublimation, it is obtained in thin plates resembling those of naphthalin, but smaller and of inferior lustre. When quite pure, it has no smell, but it is apt to retain a trace of oil, which communicates to it a faint empyreumatic odour. It is entirely devoid of taste. It is not volatile at ordinary temperatures, but is slowly volatilised in the water-bath. At higher temperatures, it sublimes freely. It melts at 416° F. into a transparent colourless liquid, which, on cooling, solidifies into a foliated crystalline mass, and at a higher temperature distils unchanged. It is insoluble in water, sparingly soluble in alcohol, but more so in ether, benzole, and the volatile oils. The alkalies are without action upon it, but sulphuric acid dissolves it, and acquires a green colour, with formation of a sulpho-acid; and nitric acid, even when moderately dilute, acts rapidly upon it. Chlorine and bromine form substitution-products.

The analysis of anthracene at first presented some difficulties. When oxide of copper was employed in the usual way, the carbon was always deficient, while chromate of lead gave an accurate result with that element, but a marked excess on the hydrogen.* Oxide of copper and chlorate of potash were therefore resorted to, and with success.

The results correspond exactly with the formula $C_{28}H_{10}$. This is precisely the constitution of a substance described some years since by Fritzsche† as a new carbo-hydrogen, obtained from coal-tar, with which also its properties closely agree. A careful comparison of the two substances made by Professor Fritzsche and myself, during a visit he paid to Glasgow some time since, satisfied us that his substance really is anthracene. The picric acid compounds of the two are completely identical, and have a fine ruby-red colour, which distinguishes the compounds in question from those obtained from the other carbo-hydrogens. An analysis of the compound obtained from anthracene, gave the formula $C_{28}H_{10}. C_{12}H_3(NO_4)_3O_2$, which is that given by Fritzsche for his compound.

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* I have had frequent occasion to observe, that in the analysis of carbo-hydrogens with chromate of lead a considerable excess of hydrogen is often obtained. I at first attributed this to impurities in the chromate, but analyses made with a pure material, specially made for the purpose, showed the same excess. I have not examined into the cause of this phenomenon.

† J. pr. Chem. lxxiii. 282.

Action of Nitric Acid on Anthracene.

Anthracene is but little acted on by cold nitric acid, but the boiling acid, even when moderately dilute, attacks it with considerable rapidity, the products depending upon the strength of the acid and the length of time during which the action is continued.

Oxanthracene $C_{20}H_8O_4$.—When anthracene is boiled for some days with nitric acid of sp. gr. 1·2, red fumes are evolved, and a resinous mass is obtained, which becomes hard and gritty on cooling. The same change may be more rapidly effected with acid of sp. gr. 1·4, but the product is then liable to be contaminated with some other compounds. The substance was washed with water, and purified by crystallisation from alcohol or benzole. It is then obtained in crystals, which, when deposited from alcohol, are long silky needles, but from benzole are shorter and more compact. They are of a light buff colour, and have neither taste nor smell; they are insoluble in water, sparingly soluble in alcohol, and more so in benzole. They are completely soluble in boiling nitric acid of sp. gr. 1·4, and are deposited unchanged on cooling. Concentrated sulphuric acid in the cold dissolves them with orange colour, which becomes deep red on heating, and on dilution with water the oxanthracene is deposited unchanged. Oxanthracene sublimes when heated, and is deposited unaltered in fine needles of considerable length. It may be distilled without decomposition over quick-lime. Its volatility may be taken advantage of as a means of preparing it, as it is only necessary to boil anthracene in a retort with nitric acid, and to continue the heat until the acid has distilled over and the oxanthracene sublimes, any other compounds formed at the same time being decomposed.

Oxanthracene is derived from anthracene by the removal of two equivalents of hydrogen, and the addition of four of oxygen. It belongs to a class of substances of which there are very few examples, and for which we have no satisfactory system of nomenclature. I have given it the provisional name of oxanthracene, as recalling its mode of formation.

Binitroxanthracene.—When anthracene was boiled for a long time with nitric acid, with occasional addition of fuming acid, red fumes continued to be given off, and a resinous substance was gradually produced. The substance was washed with water and dried. It appeared to be a mixture of some of the last substance with a new compound, which was obtained by heating it with a small quantity of alcohol, and cooling. It is deposited as a red powder which shows but little disposition to crystallise. Analysis gave results affording a distant approximation to the formula $C_{28}H_6\ (NO_4)_2O_4$, which probably represents its constitution; but as its properties showed nothing of interest, I did not prosecute its purification further.

Anthracenic Acid.—When the nitric acid and the washings of the preceding compound are carefully evaporated over the water-bath, a yellow crystalline acid is obtained. It is very soluble in water, and gives crystallisable salts with ammonia and potash, and precipitates the salts of lead and baryta. The further investigation of this substance is reserved for a future communication.

Action of Bromine on Anthracene.

Bromine acts rather slowly upon anthracene in the cold. The two substances when mixed together, concrete into a resinous-looking mass, the interior of which is not completely saturated with bromine, and it was found most convenient to expose the anthracene in a thin layer under a bell glass, along with a capsule containing bromine. After a day or two's exposure, the anthracene agglutinates into a mass which must be removed, reduced to powder, and reintroduced; and this treatment is repeated as long as bromine is absorbed. This mass, which has a brown colour, dissolves in benzole, and on cooling deposits *hexbromide of anthracene* in crystals, which are purified by solution in benzole or ether. It is thus obtained in small hard white granular crystals, apparently rhomboidal. They are sparingly soluble in alcohol, ether, and benzole. Nitric acid acts upon them but slightly. When heated with strong sulphuric acid, they fuse, and bromine and hydrobromic acid are expelled. On digestion with alcoholic potash, they immediately become yellow, and are converted into another compound.

When heated to 348° F. they become brown, and at 361° fuse and give off bromine. Analysis gave the results agreeing nearly with the formula $C_{28}H_{10}Br_6$. The substance is produced by the direct absorption of six equivalents of bromine.

Tetrabrominated Anthracene.—When the preceding compound is treated with an alcoholic solution of potash, it swells up considerably and acquires a bright sulphur-yellow colour, the solution containing bromide of potassium. This change occurs in the cold, but it is more convenient to heat the solution. The yellow powder is collected on a filter, washed, dried, and crystallized from boiling benzole. It is thus obtained in long yellow needles, having a fine silky lustre. It is very sparingly soluble in cold alcohol, ether, and benzole—more so when hot. Boiling benzole is its best solvent, but even of this it requires above a hundred times its weight. It melts at 460° F., and gives a dark-coloured mass, which has undergone partial decomposition. The portions used for analysis were crystallised from benzole, and then washed with ether.

Analysis gives for the constitution of the compound $C_{28}H_8Br_4$, a somewhat unusual formula, differing from that of most similar compounds. In general, when a bromide or chloride of an organic compound is treated with potash, one half of the haloïd is removed in combination with hydrogen, the remainder passing into the radical. In this case, however, only two equivalents of hydrogen are removed, and the formula of the compound ought in all probability to be written $C_{28}H_8Br_2 . Br_2$.

ACTION OF CHLORINE ON ANTHRACENE.

The examination of the compounds produced by the action of chlorine on anthracene is attended with some difficulty, the changes occurring being of a somewhat complicated kind; more than one substance being generally obtained, and the nature and proportion of the products depending very greatly on the circumstances of the experiment. Chlorine is readily absorbed by anthracene in the cold, and if the current is rapid, it becomes warm, gives off hydrochloric acid in abundance, and is eventually converted into a hard cake. If the chlorine be passed through it in a slow current, the evolution of hydrochloric acid is greatly diminished, although it cannot be altogether avoided; and when this is done, and the stream of chlorine is not continued too long, the principal product is:

Bichloride of Anthracene $C_{28}H_{10}Cl_2$.—The mass obtained by the action of chlorine dissolves readily in benzole, and on cooling, groups of radiating needles, often of considerable length, are deposited. The bichloride is readily soluble in alcohol, but only very sparingly in ether. When crystallised from alcohol, it is very liable to lose hydrochloric acid, and this change always takes place to some extent, which causes a slight excess of carbon and deficiency of chlorine in the analysis.

Chloranthracene $C_{28}H_9Cl$.—When anthracene is treated with a rapid current of chlorine continued for a short time only, this compound is produced. It may also be obtained by decomposing the preceding substance with alcoholic potash. It is soluble in alcohol, ether, and benzole, from the last of which solutions it is deposited in small hard scaly crystals.

When chlorine is passed over anthracene kept hot, it is absorbed in much larger quantity, and hydrochloric acid is abundantly evolved. The compounds thus obtained depend entirely on the length of time during which the current is continued, and products analysed at different periods were found to contain very different quantities of carbon and chlorine; and as the substances produced differ little in solubility, it was found difficult to effect their separation. When the passage of chlorine is continued for about eight days, the product is semisolid, and the greater part dissolves easily in cold ether; and when this solution is evaporated, first an oily chloride and then crystals are deposited. The crystals are soluble in benzole, alcohol, and ether, and were found to have a composition agreeing with the somewhat improbable formula $C_{28}H_9Cl_5$; but it is quite possible that the substance may be a mixture. The oily chloride gives more than one crystalline substance when treated with alcoholic potash.

The facts now detailed are sufficient to fix the constitution of anthracene, and to show that its chemical relations are of considerable interest. Its formula connects it with certain substances derived from oil of bitter almonds, and more especially with stilbene, the carbo-hydrogen discovered by Laurent, from which it differs by two equivalents of hydrogen. A similar relation exists between oxanthracene and benzil, as is seen by the following comparison of their formulæ:—

Anthracene, . .	$C_{28}H_{10}$	Stilbene, . . .	$C_{28}H_{12}$
Oxanthracene . .	$C_{28}H_8O_4$	Benzil, ...	$C_{28}H_{10}O_4$

XI.—*On the source of the Arsenic in the Sulphuric Acid of Commerce, and the preparation of that Acid free from Arsenic.*

By Charles L. Bloxam.

In an account of some experiments upon the electrolytic test for arsenic, published in the Society's Journal for January, 1861, it was stated that I had been unable to procure specimens of sulphuric or hydrochloric acid which did not yield any indication of arsenic when examined by that test. Although the purest samples of these acids furnished by the operative chemist contain so minute a proportion of arsenic that it could not mislead an experienced analyst engaged in a judicial inquiry, still it cannot be denied that if these most important re-agents could be declared incapable of yielding the slightest indication of the poison under the most rigorous scrutiny, greater confidence would be felt by the person eliciting, and—which is perhaps more important—by those receiving the chemical evidence in criminal cases. I therefore beg to submit to the Society the following account of experiments made to ascertain, firstly, the possibility of preparing sulphuric acid which should yield no arsenical deposit in the electrolytic test, and secondly, the source of the arsenic in the best samples of the commercial acid.

The sample of sulphuric acid selected for the experiments was taken from the ordinary laboratory supply, and contained so small a quantity of arsenic that no evidence could be obtained by Marsh's test when applied in the ordinary way, though by passing the gas through a narrow heated tube for about half an hour, a slight deposit of arsenic was obtained, and the electrolytic test gave a very decided result.

Experiments were first made upon the method generally recommended for the removal of arsenic from sulphuric acid by converting it into the volatile chloride.

1. Two measured ounces of the acid were mixed with a solution of 100 grains of chloride of sodium in six drachms of water; the mixture was boiled in a flask, the evolved hydrochloric acid gas being passed into two drachms of water. As soon as the volume of the latter had increased to eight drachms, the sulphuric acid

remaining in the flask, and the hydrochloric acid which had distilled over were examined for arsenic, which was found in them distinctly, both by the electrolytic and Marsh's test.

2. Three measured ounces of sulphuric acid were distilled with 100 grains of fused chloride of sodium. After the evolution of hydrochloric acid gas had ceased, two drachms of aqueous hydrochloric acid distilled over, containing enough arsenic to give a yellow tinge with hydrosulphuric acid. Two ounces of the sulphuric acid were then distilled over, each being received separately, but they both contained arsenic, as did also the last ounce remaining in the retort.

3. Four ounces of sulphuric acid were boiled in a flask, and the carefully washed hydrochloric acid gas, from one ounce of salt and two ounces of sulphuric acid, was passed into the boiling acid for half an hour, after which arsenic could still be distinctly detected in it.

Not having succeeded in removing the last traces of arsenic by the action of hydrochloric acid, I next endeavoured to effect it by continued electrolysis; but even after a powerful current had acted during five hours upon the acid, enough arsenic remained to convince me that this plan would be inapplicable. A process of fractional distillation was then tried.

4. Twenty measured ounces of the sulphuric acid were distilled, and the following fractions collected:—(1) 1oz., (2) 4oz., (3) 4oz., (4) 4oz., (5) 4oz., (6) ½oz., leaving about 2oz. in the retort. Each of these fractions contained arsenic, and the residue in the retort was found to contain a larger proportion than the original acid.

Half of the fifth fraction was distilled again, but the first half ounce was still found to contain arsenic, though in very minute proportion.

The remainder of the fifth fraction was distilled with bichromate of potash, in the hope of converting any arsenious into arsenic acid, but the first portion of the distillate gave evidence of arsenic.

Three ounces of the fourth fraction were rectified, the first two drachms being rejected, and 2¼oz. distilled over. This still contained a trace of arsenic, though more was found in the ½oz. left in the retort.

Two ounces of the twice-distilled acid were subjected to a third distillation, the first drachm being rejected. Ten drachms were distilled over,* and of this thrice-distilled acid two drachms gave evidence of the presence of a trace of arsenic, both by electrolysis and by Marsh's test. No satisfactory result was obtained by distilling the sulphuric acid with permanganate of potash to oxidize the arsenious acid.

My endeavours were next directed to the preparation of pure sulphuric acid from sulphurous acid gas, when I anticipated not the least difficulty in obtaining an acid perfectly free from arsenic.

1. In the first experiments, the sulphurous acid was prepared from sulphuric acid and charcoal, well washed, and oxidized by moist air with the aid of heated pumice-stone coated with platinum. This acid, however, contained more arsenic than the ordinary sample, which was traceable to the hydrochloric acid used in preparing the bichloride of platinum for platinizing the pumice. Moreover, the process was found very troublesome, and furnished too little acid in a given time to answer my purpose.

2. The sulphurous acid, prepared from sulphuric acid and copper,† was very well washed, and oxidized by means of air, steam, and nitric oxide (prepared from nitric acid and copper), in a glass globe, the sulphuric acid being afterwards boiled down in a platinum dish. A trace of arsenic was also found in this specimen.

3. The copper employed in the preceding experiment having been found to contain much arsenic, mercury was next employed for evolving sulphurous acid, but still a trace of arsenic was found in the sulphuric acid produced, and accompanying it was a minute quantity of mercury.

4. Believing it possible, from the result of the last experiment, that the high temperature employed in preparing the sulphurous acid expelled arsenic from the acid in the generating flask, and that washing was incapable of removing the last traces of arsenic from the gas, I next evolved the sulphurous acid at a far lower temperature from crystallized sulphite of soda by the action of sulphuric acid, and in this case it was but just possible to demonstrate the presence of a trace of arsenic. Three trials of this

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* It may be worth notice that the residual acid in the retort contained a considerable quantity of platinum in several of these distillations, a piece of platinum foil having been used to prevent bumping.

† The formation of free sulphur and of sulphide of copper was well observed in preparing the large volume of sulphurous acid required in these experiments.

method having given the same result, it was thought that the trace of arsenic might be derived from the copper employed in evolving the nitric oxide.

5. In this experiment, the nitric oxide was prepared from nitre by the action of sulphate of iron and dilute sulphuric acid at a very moderate heat, whilst the sulphurous acid was disengaged as before from sulphite of soda and sulphuric acid.* The resulting sulphuric acid was found to yield not the least indication of arsenic when tested by electrolysis.

Having satisfied myself that it was possible to obtain sulphuric acid which furnished no indication in the electrolytic test, I proceeded to look for the source of the arsenic in the purest specimens of the commercial acid.

By the kindness of the manufacturer, I was supplied with a sample of the Sicilian sulphur employed in the manufacture of one of the purest sulphuric acids, in which, however, the electrolytic test, as well as a prolonged application of Marsh's test, indicated the presence of a trace of arsenic.

This Sicilian sulphur was burnt in air, and the sulphurous acid obtained was converted into sulphuric acid in precisely the same manner as in the last of the experiments above described as giving an acid free from arsenic. The sulphuric acid thus prepared from the Sicilian sulphur gave distinct evidence of the presence of arsenic. A repetition of the experiment with a fresh portion of the sulphur gave the same result.

In order to be quite sure that the arsenic had been derived from the sulphur, I burnt 500 grains of the sulphur, when it left about a grain of a black residue consisting chiefly of sulphide of iron. This was dissolved in a very little nitro-hydrochloric acid; the diluted solution was saturated with hydrosulphuric acid and boiled, when a slight dirty yellow precipitate fell; this was treated with ammonia, which dissolved the yellow portion, leaving a few black particles which proved to be sulphide of lead. The ammoniacal solution, when evaporated, left a yellow residue, which was dissolved in nitric acid; on evaporating the acid and testing with nitrate of silver, the characteristic precipitate of arseniate of silver was obtained.

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* I found it advisable, for obvious reasons, to dispense with the use of caoutchouc connectors in the tubes immediately leading to the globe in which the gases were mixed, and to employ a perforated glass plate instead of a cork, for closing the mouth of the globe.

It is evident, therefore, that the sulphur under examination contained a minute proportion of arsenic, part of which passed off with the sulphurous acid when the sulphur was burnt, whilst the remainder was found in the residue with the sulphides of iron and lead.

Though it cannot be inferred, from the examination of a single sample, of the identity of which I have no direct evidence, that Sicilian sulphur always contains arsenic, such an inference is greatly favoured by the circumstance that this impurity has been detected in the specimens of sulphuric acid manufactured with every precaution to insure its absence.

The conclusions to which I have been led by the above experiments are:—

1. That sulphuric acid cannot be completely purified from arsenic either by hydrochloric acid or chloride of sodium, or by repeated distillation, whether alone or with bichromate or permanganate of potash.

2. That the minute quantity of arsenic found, even in the purest samples of commercial sulphuric acid, is derived from the native sulphur employed in its manufacture.

3. That when sulphuric acid is required which shall yield no indication of arsenic to the electrolytic test, the sulphurous acid and nitric oxide employed in its preparation must be evolved at as low a temperature as possible, since the fumes which accompany the gases prepared by the ordinary methods, and are not completely removed by washing, bring over small quantities of arsenic.

It is very probable that experiments conducted upon a manufacturing scale would lead to an easier process for obtaining the sulphuric acid in a state of absolute purity.

Note.—In a former communication, I have stated that arsenic acid does not respond to the electrolytic test. This is not strictly correct, the result depending upon the presence or absence of hydrochloric acid,* although, even when that acid is not present, arsenic acid, as might be expected, does not yield arseniuretted hydrogen so rapidly as arsenious acid. Three experiments were made with pure arseniate of magnesia and ammonia dissolved in dilute sulphuric acid. A quantity of this solution corresponding to 0·1 grain of arsenious acid gave an immediate deposit of metallic arsenic in the heated reduction tube; one-tenth of that quantity gave a deposit in seven minutes (though not so much as would have been furnished by arsenious acid), and a quantity representing 0·001 grain of arsenious acid gave a deposit in twenty-one minutes.

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* Since, in the practical application of the electrolytic test to the detection of arsenic in organic mixtures, hydrochloric acid is always present, the addition of sulphurous or hydrosulphuric acid, as formerly recommended, is still necessary. It was while endeavouring to discover, by electrolysis, the state of oxidation of the arsenic in sulphuric acid, that the reduction of arsenic acid in the absence of hydrochloric acid was noticed.

XII.—*Note on the Composition of a Boiling Spring in New Zealand.*

By Professor Smith, University of Sydney.

Stretching in a north-easterly direction from Taranaki, in the north island of New Zealand, is a line of volcanic action, terminating in White Island, in the Bay of Plenty. In this line are numerous solfataras, boiling springs, basins of seething mud, and hot lakes, presenting, in some localities, scenes of remarkable beauty and grandeur. Some of the boiling springs are intermittent jets, of the same character, though not of the same magnitude, as the geysirs of Iceland. The New Zealand springs have, in many cases, formed terraces and incrustations of siliceous matter, probably unsurpassed, in extent and magnificence, by any similar deposits in the world. One of the most copious of the boiling pools is named "Te Tarata." It is on the shore of Rotomahana ("Hot Lake"), at an elevation of some fifty feet. The water is of a beautiful pale blue colour. It descends to the lake in a series of cascades over the edges of extensive basins and terraces of siliceous deposit. On the occasion of my visit, the water was in violent ebullition, the temperature being a little above that of pure water boiled at the same place. I carried a bottle of it with me to Sydney, and made an analysis of it about a month after its collection. The specimen was then milky, and had a slight smell of sulphuretted hydrogen. Taste soft and unpleasant. It was highly alkaline to test paper. Specific gravity 1·00205. A slight sediment had fallen, which seemed to be chiefly vegetable matter. The quantity of water in my possession was too small for a complete and unexceptionable analysis, but the following Table gives, I believe, a tolerably close approximation:—

	Grains per Gallon.
Silica..	42·40
Soda (probably combined with silica) ..	16·00
Chloride of sodium	113·57
Chloride of potassium	6·67
Sulphate of potash	5·28
Carbonate of lime	1·76
Alumina	0·32
Magnesia and iron	traces
	186·00
Total solid matter obtained by evaporation at 212° F...	189·12
Matter volatilized by ignition	4·00
Leaving for fixed salts	185·12

The arrangement of acids and bases is of course, to a considerable extent, matter of opinion. There being only a small amount of carbonic acid present (not directly estimated), I assume that it is just sufficient to supply the lime. The sulphuric acid found (2·42 grs.) is given to potash, the remainder of the potassium being supplied with chlorine. The potassium (calculated from the precipitate by bichloride of platinum) amounted in all to 5·87 grns. The whole chlorine was 72 grns. There is a residue of soda which, I suppose, may be combined with silicic acid. There could have been no sulphide of sodium present, for the precipitate with nitrate of silver was white, and there was no escape of sulphuretted hydrogen on adding hydrochloric acid to the dry residue obtained by evaporation. Boracic acid was tested for, but none found.

In a bottle of water that I afterwards obtained from the same locality, though, perhaps, not from the same spring, I found solid matter at the rate of 178·8 grns. per gallon. Of this the silica amounted to 57·08 grns., 30·08 grns. being in a state of solution, and 27 grns. having separated as a yellowish-white gelatinous sediment. The chlorine amounted to 70 grns. per gallon.

I examined the white incrustation upon reeds and other objects immersed in the spring. It was silica, with traces of common salt, lime, and alumina. Dried at 212° F., it lost 2·26 per cent. of its weight. On ignition, there was a further loss of 5·05 per cent., making altogether a loss of 7·20 per cent., calculated on the air-dried powder.

XIII.—*On the Solubility of Sulphate of Lead in Hydrochloric and Nitric Acids.*

By George F. Rodwell.

Perfectly pure and dry sulphate of lead was digested, at ordinary spring and autumn temperature, with the different strengths of hydrochloric and nitric acids given below, in well-stoppered bottles, the mixture being frequently shaken. The time of digestion varied from one to ten days. Determinations of the amount of sulphate of lead dissolved were made on each intermediate day, but it was found that the maximum amount was, in every instance, dissolved before the fifth day of digestion.

The sulphate of lead was allowed a night to settle down; the required quantity of the solution was then filtered off, weighed, and transferred to a porcelain crucible; a few drops of dilute sulphuric acid were added; the solution was evaporated to dryness over a water-bath, and heated in an air-bath to expel sulphuric acid, with the lid on the crucible; and the residue was ignited, allowed to stand in dry air just long enough to cool (previously determined), and immediately weighed.

It was found impossible to evaporate the more concentrated solutions of sulphate of lead in hydrochloric acid over the water-bath: for, when the evaporation was about a third effected, a scum of chloride of lead formed on the surface, and the bubbles of hydrochloric acid, rising from the bottom, burst at the surface of the liquid, throwing particles of the scum outside the crucible, although it was not half full. The evaporation of such solutions was therefore completely effected in an air-bath, the lid being placed on the crucible to prevent the possibility of a particle escaping.

Twenty determinations of the amount of sulphate of lead dissolved by each different strength of hydrochloric and nitric acid were made: the best four and their mean are given.

The following results were obtained:—

100 parts of dilute hydrochloric acid, of the specific gravities given below, dissolve severally of sulphate of lead,—

1. Specific gravity 1·0519 = 10·602 per cent. HCl.
·1468, ·1466, ·1467, ·1465
Mean = ·14665.

On diluting the solution with water, no change was apparent.

2. Specific gravity 1·0800 = 16·310 per cent HCl.
·3546, ·3537, ·3558, ·3557,
Mean = ·35495.

On diluting the solution with water, a few minute needles of chloride of lead came down on standing.

3. Specific gravity 1·107 = 22·0100 per cent. HCl.
·9483, ·9444, ·9476, ·9458,
Mean = ·946525.

On diluting the solution with water, needles of chloride of lead came down.

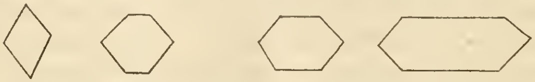
4. Specific gravity 1·1359 = 27·5245 per cent. HCl.
2·1169, 2·1141, 2·1121, 2·1122,
Mean = 2·113825.

On diluting the solution with water, needles of chloride of lead at once came down.

5. Specific gravity 1·1570 = 31·6015 per cent. HCl.
2·8549, 2·8508, 2·8553, 2·8588,
Mean = 2·85495.

On diluting the solution with water, an immediate and abundant precipitate of needles of chloride of lead was thrown down.

If a solution of sulphate of lead in hydrochloric acid be evaporated, we get, on cooling, a number of crystalline plates of pearly lustre. They consist of chloride of lead, and are of the following forms:—



If these plates are dissolved in a small quantity of hot water, *needles* of chloride of lead are deposited on cooling.

When a concentrated solution of sulphate of lead in hydrochloric acid is slowly evaporated, at the rate of about a gramme in two hours, we find that rhombic plates of chloride of lead are first formed. As the evaporation proceeds, however, the small quantity of sulphuric acid present, becoming more concentrated, slowly decomposes these crystals, and we get sulphate of lead in rhombic plates

100 parts of dilute nitric acid, of the specific gravities given below, dissolve severally of sulphate of lead,—

1. Specific gravity 1·079 = 11·55 per cent. NO_5.
·3303, ·3295, ·3300, ·3299,
Mean = ·329925.

2. Specific gravity 1·123 = 17·5 per cent. NO_5.
·5748, ·5763, ·5754, ·5756,
Mean = ·575525.

3. Specific gravity 1·25 = 34 per cent. NO_5.
·7832, ·7835, ·7854, ·7855,
Mean = ·7844.

If any of these solutions are evaporated, we obtain, on cooling, octohedra of nitrate of lead.

4. Specific gravity 1.42 = 60 per cent. NO_5.
·0098, ·0097, ·0097, ·0097,
Mean = ·009725.

If this solution be evaporated to about $\frac{1}{12}$th of its bulk, a small quantity of powder is deposited, which is seen, under the microscope, to consist of octohedra of nitrate of lead.

When sulphate of lead is digested with nitric acid containing 60 per cent. NO_5, it is found, after three or four days, to be almost entirely converted into octohedra of nitrate of lead. On continuing the digestion for twenty-one days, a minute quantity of sulphate still remained unconverted.

From the above results, we see that 1 part of sulphate of lead is soluble, at the ordinary temperature, in—

Dilute Hydrochloric Acid.	Spec. Grav.		Per Cent. HCl.
681·8956 parts	1·0519	=	10·602
281·7298 ,,	1·0800	=	16·310
105·6496 ,,	1·1070	=	22·010
47·3076 ,,	1·1359	=	27·5245
35·0268 ,,	1·1570	=	31·6015

Dilute Nitric Acid.	Spec. Grav.		Per Cent. NO_5.
303·0991 parts	1·079	=	11·55
173·7542 ,,	1·123	=	17·50
127·4859 ,,	1·250	=	34·00
10282·7763 ,,	1·420	=	60·00

XIV.—*On the Resin of* Ficus rubiginosa, *and a new Homologue of Benzylic Alcohol.*

By Warren De la Rue, Ph.D., F.R.S., Treasurer of the Chemical Society, Secretary of the Royal Astronomical Society, &c., and Hugo Müller, Ph.D., F.C.S.

(Abstracted from the Philosophical Transactions, 1860, Part I.)

Among the interesting collection of natural products contributed to the Paris Universal Exhibition of 1855 by the British Colonies, was a gum presenting some remarkable qualities. This substance was stated by the exhibitor to be a new species of gutta percha, in consequence of its becoming plastic when masticated, and on this account it attracted considerable attention. It had been contributed by Dr. Stephenson, of Manning River, N.S.W., who had obtained it from a species of *Ficus*, known as *F. rubiginosa.* The zealous Commissioner for New South Wales, Mr. (now Sir William) Macarthur, brought this gum under our notice, with the view of obtaining some information respecting its chemical properties.

A few preliminary experiments, which were made in Paris, at once showed us that this substance had very little in common with gutta percha, and, moreover, its chemical properties were found to be entirely different from those of that gum. Although our experiments did not allow us to hold out hopes to Mr. Macarthur of the gum becoming a valuable article for exportation from the colony, they offered some inducement to us to make a more rigorous investigation of it on purely scientific grounds. On communicating this view to Mr. Macarthur, he liberally placed at our disposal the remainder of the specimen exhibited.

In pursuing subsequently the study of this subject, we discovered one of the proximate constituents to be a natural acetic ether of a new radical homologous to benzyl (C_7 H_7). The peculiar interest which attaches to this class of compounds, induces us to bring under the notice of the Society the results of our investigation.

This gum or resin exhibits, on the first glance, great similarity in its general appearance to "Gum Euphorbium," occurring, like that substance, in irregular pieces, generally pierced with holes; some specimens also exhibiting a stalactitic formation. The holes in the fragments of this resin are produced by a small beetle of the tribe "Curculio," which apparently feeds upon, and lives in this resin, as it oozes in a semifluid state from the branch of the tree. We had no means of ascertaining whether or not this insect causes the secretion of the resin by puncturing the branches of the tree, in the same manner as the *Coccus ficus* does for the purpose of depositing its ova. The colour of the gum varies from a dirty yellow or red, almost to white. It is solid and brittle, but some of the larger pieces exhibit, especially in the interior, a degree of toughness which renders it difficult to powder. It is opaque, the fracture being dull and wax-like.

At a temperature of about 30° C. (86° Fahr.) this resin becomes soft, when it resembles gutta percha, being plastic without becoming sticky, provided it has been previously wetted with water. In its natural condition, it has neither taste nor odour; but when heated, it evolves a wax-like odour, and on being masticated evinces a characteristic taste.

In hot or cold water it is perfectly insoluble; but warm alcohol, ether, oil of turpentine, and other solvents of resinous substances dissolve it with facility. Solutions of caustic alkalies have no effect on it, even when aided by heat.

When left for some time in contact with cold alcohol of ordinary strength, the greater part of the resin is dissolved, whilst a white flocculent substance remains undissolved. By employing this solvent, we succeeded in separating several distinct classes of substances from the Ficus resin. The constituent, readily soluble in cold alcohol, formed an amorphous resinous substance, when separated from the solvent by distillation or precipitation with water. The white insoluble part, when further treated with boiling alcohol, is in part dissolved, particles of bark, sand, and other accidental impurities remaining undissolved. The alcoholic solution of the white substance deposits, on cooling, a white crystalline mass, which by repeated crystallization may be obtained in beautiful scaly crystals. From the residue insoluble in boiling alcohol, bisulphide of carbon or chloroform extracts a small quantity of caoutchouc.

A quantitative experiment by the above method yielded the following approximate per-centage result:—

Resinous substance, readily soluble in cold alcohol .	73
White crystalline substances, insoluble in cold alcohol, but soluble in warm alcohol . . .	14
Caoutchouc, fragments of bark, sand, and loss .	13

The resinous substance, readily soluble in cold alcohol, which forms, according to this analysis, by far the principal constituent of our resin, offered but little inducement for chemical investigation. However, a number of experiments were made, which, although unproductive in their results, may serve to characterize this substance, which possesses peculiarities distinguishing it from other bodies of like origin. In order to identify it hereafter, we propose to call this resin Sycoretin. At the same time, we must state that we were not successful, for reasons hereinafter mentioned, in obtaining this substance perfectly pure.

Sycoretin.

Cold alcohol of moderate strength dissolves the principal part of the original resin, forming a light brown solution, which on precipitation with water, or the separation of the alcohol by distillation, yields the sycoretin. The alcoholic solution of this resin is perfectly neutral, and scarcely any precipitate is caused in it on the addition of an alcoholic solution of acetate of lead or acetate of copper. This behaviour indicated at once that no acid compounds were present, and that the resin is perfectly neutral. The minute precipitate which formed we ascertained to be tannate of lead, the source of the tannic acid being probably the bark which contaminated the resin. This resin was purified by redissolving it in alcohol, and in order to remove the small amount of colour, the solution was treated with animal charcoal, but this had no effect. No better result was obtained when a small quantity of acetate of lead was introduced into the solution, and a basic lead-salt thrown down with ammonia. We afterwards found that the colour could be gradually removed by repeated precipitation of the resin from its alcoholic solution by water.

The decolorized resin was now redissolved in a just-sufficient quantity of alcohol, and the solution left for some time in a cool place, when a small amount of crystalline substance was deposited, which was filtered off. By addition of a little water, a small quantity of sycoretin was then thrown down, in order to carry down the last traces of the less soluble crystalline compound, in case any were still present. After this treatment, the solution was again allowed to stand for some time, but no further precipitate was formed. The clear solution was now partly precipitated with water, and the precipitate removed after it had subsided, heat being used to facilitate the subsidence of the sycoretin by causing the precipitate to agglutinate into one mass. That part of the resin remaining in solution was afterwards thrown down with water and collected separately.

The two different lots of resin thus obtained had the same appearance; both were brittle, but only the last became sticky when masticated, and tasted like the original resin. Both products were powdered and kept for some time *in vacuo* over sulphuric acid, in order to remove all traces of any adhering water or alcohol.

The analysis of the first precipitated part (A) gave the following per centages :—

Carbon .	. 74·65	Hydrogen .	. 10·11

The analysis of the portion last thrown down (B) gave the following per-centages :—

Carbon .	. 77·89	Hydrogen .	. 9·94

It will be observed from the preceding numbers, that the resin, which has the property of agglutinating on being masticated, is richer in carbon than that first thrown down by water from the alcoholic solution. The peculiar characters of these substances did not, however, permit of any formulæ being determined for them.

Sycoretin is almost white; it is very brittle. It melts in boiling water to a thick liquid, floating on the surface, and when powdered becomes so electric that it flies out of the mortar. In water, dilute acids, alkaline solutions, or ammonia, it is insoluble; but it is readily soluble in alcohol, ether, chloroform, oil of turpentine, &c.

In order to ascertain whether sycoretin was allied to that class of bodies called glucosides (jalapin, for example), the following experiments were made :—

Action of Sulphuric Acid on Sycoretin.

A portion of the sycoretin, prepared, as stated above, by fractional precipitation, was added to concentrated sulphuric acid; it was readily dissolved, forming a fine deep red solution, which gave off only a faint odour of sulphurous acid when kept for several days. By exposure to the air, or on addition of water, a brownish precipitate deposited, which differed from the original solution by its lesser solubility; the aqueous liquid contained a trace of a sulpho-copulate acid, but no saccharine substance could be discovered. Analogous results were obtained by treating it with a concentrated solution of potash. These experiments show that sycoretin cannot be classed with the glucosides; moreover, all attempts to place this substance in connexion with some of the classified organic compounds were unsuccessful, and we are therefore constrained to leave it for the present among the so called resins, under which term are comprised all sorts of bodies, acid and neutral, which have nothing in common except some physical resemblance.

Action of Nitric Acid on Sycoretin.

It appears that the only products of the action of concentrated nitric acid, are a peculiar nitro-compound and a small quantity of oxalic acid, no picric acid being formed.

On submitting sycoretin to the action of nitric acid, the powdered resin was introduced in small quantities into the acid at the ordinary temperature, and when the action had somewhat subsided, the acid was boiled for some time, when every particle of resin disappeared. The resulting yellow liquid was mixed with water, when a copious precipitate of a pale yellow colour was formed. The precipitate was filtered off, and washed with water. The filtrate, when freed from nitric acid by evaporation, gave an additional precipitate of the nitro-compound on admixture with water. The nitro-compound has slightly acid properties, and is readily soluble in solutions of potash and ammonia. Carbonate of potash also dissolves it, but there is no evolution of carbonic acid, even when the solution is warmed. All the solutions in alkalies are dark yellowish brown, and leave on evaporation an amorphous residue. Lead and other metallic salts give coloured precipitates with its solution, but, as might be expected, no definite compounds could be produced in this way. The compound with potash, when heated on platinum-foil, melts, takes fire, puffs up, and burns with the vivacity of other nitro-compounds.

Action of Heat on Sycoretin.

When heated in a retort, sycoretin melts below 100° C. and, at a temperature of a few degrees higher, froths considerably, giving off water which retains the peculiar odour perceptible on heating the original resin. On raising the temperature much higher, it becomes quiet, and begins to decompose, giving off at first a mobile liquid, and towards the end a dark yellow tar-like substance, leaving only a small quantity of charcoal behind. The distillate so obtained has a disagreeable smell, somewhat like burnt india-rubber, acetic acid being also present in considerable quantity.

By treating it with a solution of carbonate of sodium, the acetic acid is removed, a dark brown oily liquid remaining, which possesses now a less disagreeable odour. This oily liquid, submitted to a new distillation, gives at first a very mobile liquid, possessing in every respect the properties of caoutchin, and then a thick oily liquid, which soon becomes dark brown when exposed to the air.

Acetate of Sycoceryl.

We assign this name, for reasons hereafter to be mentioned, to the crystallizable substance, which, as already mentioned, is obtained when the residue, left after the treatment of the original resin with cold alcohol, is dissolved in boiling alcohol, and the solution allowed to cool.

For the preparation of this substance, the original resin is coarsely powdered and extracted with cold alcohol, in order, as far as possible, to remove the sycoretin. The undissolved residue is then exhausted with boiling alcohol. The several solutions thus obtained are filtered and allowed to cool, when a white deposit is formed, which generally shows but little indication of crystallization. This white deposit is again dissolved in a large quantity of boiling alcohol, and left in a quiet place to cool slowly, when a more perfect crystallization is obtained.

Towards the latter part of the crystallization, a substance is deposited of different appearance, being of a more flocculent nature, and altogether different from the crystals first deposited. This substance is present only in very small quantity, and its separation from the other crystallizable constituents of the resin is attended with great difficulties. In order to effect this separation, the alcoholic solution is allowed to cool to about 40° C. (104° Fahr.), and then the crystals which may have formed are separated by straining off the liquor as quickly as possible through a piece of gauze. The mother-liquor, on further cooling, will now deposit the flocculent substance, contaminated, however, with the first substance. By repeating this operation, a perfect separation of this second substance may be effected.

By repeated solution in and recrystallization from hot alcohol, the crystalline substance (acetate of sycoceryl), was obtained perfectly white and transparent and apparently pure. An examination with the microscope, however, proved that another foreign body had deposited in smaller crystals on the faces of the supposed pure substance. This new body proved to be much less soluble in different vehicles than our acetate of sycoceryl, but, being present only in very small quantity, its separation caused us at first very great perplexity, but finally we found the following method perfectly efficacious for that purpose.

The dry crystals were placed in a flask, and a quantity of ether insufficient to dissolve the whole substance was introduced, the temperature being maintained at about 30° C. (86° Fahr.); more ether was cautiously added from time to time until the larger crystals had just disappeared, leaving the smaller ones of the new substance undissolved. The separation of the two substances is not, however, perfect in a single operation; for when the flask is allowed to cool, a small part of this parasitical body deposits. After distilling the filtered etheric solution, the acetate of sycoceryl is obtained in a state of perfect purity, and by recrystallization from alcohol, ether, or chloroform, it may be procured in beautiful crystals.

Acetate of sycoceryl so obtained is perfectly colourless, and crystallizes from ether in flat prisms, which generally appear as six-sided plates. When crystallized from alcohol, the crystals are thin and scaly like mica, and have the greatest resemblance to cholesterin.

Acetate of sycoceryl is brittle, yet difficult to powder, on account of its becoming highly electric when triturated. It melts at 118°—120° C. (244°·4—248° Fahr.), and is still fluid when cooled down to 80° C. (176° Fahr.). It solidifies at first to a transparent mass, which, however, after a short time, becomes opaque and crystalline, especially if scratched with a hard body. Heated considerably above its melting-point, it boils and distils, almost without decomposition. The distillate is at first liquid, but solidifies after some time, and becomes gradually crystalline. When not perfectly pure, or if the heat is applied too rapidly, it gives out a rancid odour, in which that of acetic acid is recognizable. Hot alcohol, ether, chloroform, benzol, acetone, oil of turpentine, and concentrated acetic acid dissolve the acetate of sycoceryl with great facility. The alcoholic solution is perfectly neutral, and gives no precipitate with alcoholic solutions of the acetates of lead or copper.

Sulphuric acid dissolves it readily, forming a viscid colourless solution, which gets gradually brown, and then gives off traces of sulphurous and acetic acids. When the sulphuric solution is mixed with water, a substance is thrown down which is perfectly hard at common temperatures, but melts below 100°C. (212° Fahr.), and is very difficultly soluble in alcohol, but readily so in chloroform and benzol.

Nitric acid, when diluted, has no effect, at ordinary temperatures, on acetate of sycoceryl; but if warm, it evolves nitrous fumes, and produces a yellow resinous compound. Fuming nitrous acid, however, dissolves it readily at ordinary temperatures, giving a yellow solution from which water throws down a flocculent amorphous yellow nitro-compound.

Hydrochloric acid has no effect on acetate of sycoceryl.

Chlorine, bromine, and iodine in contact with this substance act upon it with violence, especially the two first-named reagents; the products, however, procured in this manner are only resin-like compounds not adapted for analysis.

If, however, a warm alcoholic solution of the acetate of sycoceryl is employed, and the bromine or iodine also added in solution, and in small quantities at a time, the colour of these two reagents disappears, and after cooling, a new bromo- or iodo-compound, as the case may be, is deposited in small crystals. The iodine-compound is yellow, the bromine-compound colourless. The purification of these two promising compounds, and their separation from the unaltered original substances, and another resinous body formed at the same time, was unfortunately not possible with the limited quantity of material that could be devoted to their preparation.

Solution of potash, even when boiled for a long time with the substance under consideration, does not act upon it. If hydrate of potash, however, is melted with it, a decomposition takes place, and if the temperature is raised, some hydrogen is given off. The product of this reaction, treated with water, leaves behind a colourless amorphous body, which could not be obtained in a crystalline state, or sufficiently pure for analysis. The alkaline mother-liquor saturated with diluted sulphuric acid became slightly turbid, and the presence of acetic acid was then perceptible. Soda-tartrate of copper gave no reaction indicating the presence of sugar in the solution.

Thus far we did not succeed in producing any derivative which would throw light upon the theoretical composition of our substance, and furnish us with the means of ascertaining its rational formula.

Analysis gave numbers which agree with the empirical formula $C_{10}H_{16}O$,* our substance being accordingly isomeric with camphor, to which, however, it has no further resemblance.

This composition varies also widely from that of the crystalline substances procured from analogous sources, and which have a great resemblance to our substance,—for instance, the crystalline resins on the one hand, Chinese wax and waxes generally on the other.

We have mentioned above, in speaking of the action of various reagents on our new substance, the occurrence of acetic acid under two different circumstances; we did not attach much importance to this fact at the time, because this acid occurs so frequently among the products resulting from the breaking up of organic substances; nevertheless, we subsequently repeated these experiments on a somewhat larger scale, chiefly, however, with the view of studying the other products of decomposition which are formed. In order to eliminate as much as possible the effect of temperature, we made use of that powerful reagent, the so-called "sodium-alcohol," which is obtained by dissolving sodium in absolute alcohol. Sodium-alcohol and potassium-alcohol at ordinary temperatures are, for the most part, equivalent in their reactions to the hydrates of those alkalies when in a state of fusion, and hence present the advantage of effecting decompositions in a more simple manner, the effect of a high temperature not interfering with the final result, as is sometimes the case when the fusing hydrated alkalies are employed.

Some experiments of this kind, performed with great care, convinced us that the occurrence of acetic acid could not be attributed to the effect of empyreumatic decomposition, but that it actually existed as an integral proximate constituent of our crystallizable substance. This led us at once to suspect that our substance was in reality an ether-like compound. This supposition was confirmed by the separation of a body which might be considered as the hydrated oxide of a radical; moreover, we were ultimately enabled to give the fullest confirmation to this theoretical speculation, by actually producing the original substance in a manner suggested by this view.

It should be stated that sodium-alcohol dissolves our substance with the greatest facility, and even at a temperature of 30° C.

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* Carbon = 12 Oxygen = 16.

(86° Fahr.) decomposition takes place, the reaction being unaccompanied by the evolution of gas. On cooling, the solution continues liquid, although a large quantity of the substance may have been employed; but on addition of water, a white flocculent substance separates from the colourless alkaline mother-liquor.

The flocculent substance is insoluble in water, but readily soluble even in cold alcohol. When it is dissolved in a quantity of boiling alcohol, just sufficient to take it up, the solution on cooling solidifies completely to a mass of beautiful silky crystals, quite different from those of the original substance: this new derivative proved to be the new alcohol, which we propose to call Sycocerylic Alcohol.

The aqueous liquor from which the flocculent precipitate was separated, remains almost perfectly clear, on saturation with a mineral acid; on examination, no other product besides a volatile organic acid could be found in it. The existence of a volatile acid with the odour of acetic acid, was rendered evident by saturating the alkaline mother-liquor with phosphoric acid and distilling; the distillate was saturated with carbonate of barium and evaporated to the crystallization point, when prismatic crystals, of the characteristic form of acetate of barium, were obtained. A barium determination gave numbers which agree with the formula, $C_2 H_3 BaO_2$.

Alcohol of Sycoceryl.

The preparation of this substance has been already detailed. In order to render it pure, it is only necessary, after it has been precipitated from the solution of sodium-alcohol, to wash it well with water in order to remove all traces of fixed alkali; then to crystallize it a few times from warm alcohol. The crystals usually occur aggregated in spherical masses, like the mineral Wavellite; they are very thin, and have a great resemblance to caffeine.

In several instances, during the earlier stages of its purification, or when dilute alcohol is employed for its solution, it was noticed that the substance did not deposit in crystals, but the transparent liquid congealed to a jelly. This jelly, however, after some time became crystalline, the crystallization commencing in several points of the mass, and extending gradually throughout the whole; ultimately a crystallization was obtained of the same appearance as occurs under other circumstances.

In the determination of the rational formula of this substance, we took cognizance of the fact, that, besides acetic acid, it was the only other product obtained in the decomposition of the original compound which we have denominated acetate of sycoceryl, and the analysis of which led to the empirical formula $C_{10}\,H_{16}\,O$.

From the nature of this compound, we inferred that it contained the radical of acetic acid in a state similar to that in which it exists in acetic ether; that, in fact, we had to deal with a compound containing acetic acid minus one atom of hydrogen and a radical. According to this view, the empirical formula $C_{10}\,H_{16}\,O$ would have to be doubled, whereby we obtain

$$\begin{array}{ll} & C_{20}\,H_{32}\,O_2 \\ \left.\begin{array}{l}\text{and if we now deduct the elements} \\ \quad\text{of acetic acid minus hydrogen}\quad .\end{array}\right\} = & \underline{C_2\;\;H_3\;\;O_2} \\ \text{we have} & C_{18}\,H_{29} \end{array}$$

for the radical of our new alcohol, whose formula would consequently be $C_{18}\,H_{30}O$.

The analysis of the supposed alcohol obtained from acetate of sycoceryl gave results which support this view.

According to the formula $C_{13}\,H_{30}\,O$, the new alcohol would be homologous with benzylic alcohol obtained from "oil of bitter almonds."

Alcohol of sycoceryl is perfectly insoluble in water, the fixed alkalies, and ammonia; but alcohol, especially when warm, also ether, benzol, chloroform, and naphtha, are good solvents for it.

At a temperature of about 90° C. (194° Fahr.), sycocerylic alcohol melts to a liquid heavier than water, and solidifies on cooling to a crystalline mass, especially if any fragments of crystals have remained unfused, because they become the foci of a new crystallization. When, however, the heat is increased only a little beyond the fusion point, it remains perfectly transparent and amorphous. By contact with alcohol, this glassy condition is changed to the normal crystalline structure. When it is heated considerably above its melting-point, a portion distils unchanged, and a brownish residue is left in the retort.

Potassium brought in contact with this substance when in a state of fusion, disengages hydrogen, and becomes covered with a white crust; but when heat is applied in order to fuse the so-formed potassium-compound of the sycocerylic alcohol, the reaction becomes so violent that the mass blackens and even catches fire.

Heated with hydrate of potash above the melting-point of the latter, it evolves hydrogen and decomposes; it appears that this reaction does not stop with the probable formation of an acid which unites with the potash, but goes further; for in the product of this reaction we did not find the expected acid; but it is our intention to pursue this subject if ever we are so fortunate as to procure a larger supply of material.

Concentrated sulphuric acid easily dissolves sycocerylic alcohol with evolution of heat, forming a brown liquid which remains unaltered for some time. The liquid yields, on addition of water, a resinous viscid substance, which melts at the temperature of boiling water, and is but very sparingly soluble in alcohol. Ether and chloroform dissolve it with facility, and, on evaporating, merely leave the resinous product in its original amorphous state. The aqueous liquor, saturated with carbonate of barium, gave no indications of the presence of a conjugated sulphuric acid.

Chlorine, bromine, and iodine act readily on sycocerylic alcohol: if solutions of these reagents are used, crystalline compounds are formed. The iodine-compound is of a yellow colour.

Action of Chloride of Phosphorus on Sycocerylic Alcohol.

For the purpose of preparing the chloride of sycoceryl, we employed pentachloride of phosphorus and a solution of sycocerylic alcohol in benzol. At common temperatures, no reaction took place, but when the temperature was raised to about 60° C. (140° Fahr.), hydrochloric acid was given off, and the pentachloride gradually disappeared. After the disengagement of hydrochloric acid had ceased, the liquid was removed from the remaining pentachloride and washed with water, and afterwards with an alkaline solution. After the benzol had been got rid of by keeping the liquid for some time in a warm place, a viscid residue was obtained, which was soluble with great difficulty in alcohol, but easily soluble in ether or chloroform. These solutions, after evaporation, deposited this substance again in its original sticky state. In the first experiments, which were carried out only on a very small scale, a crystalline substance was formed besides the amorphous greenish compound. This crystalline substance differed in its properties from the original alcohol. It therefore seems probable that a slight excess of pentachloride (or the phosphoric acid formed during the reaction) destroys to a great extent the chloride of sycoceryl formed during the reaction; or at all events, phosphate of sycoceryl, which is produced simultaneously and predominates, cannot be separated from the chloride. We are therefore at present unable to give a description of the chloride of sycoceryl in its pure state.

Benzoate of Sycoceryl.

Chloride of benzoyl dissolves with the greatest facility a large quantity of sycocerylic alcohol at common temperatures, but no hydrochloric acid is disengaged; probably, therefore, no reaction takes place at ordinary temperatures, but if heat is applied, the liquid soon commences to give off hydrochloric acid. When the evolution of hydrochloric acid has ceased, the mixture is allowed to cool, when it solidifies to a fibrous crystalline mass. Any excess of chloride of benzoyl is removed after the reaction by throwing the mixture into a solution of bicarbonate of potassium, whereby a resinous mass separates. The whole being kept warm for several hours, all the chloride of benzoyl is decomposed. During this process, a slight smell, somewhat like benzoate of ethyl, is perceptible. The resinous mass, after removal from the saline liquors, is washed several times with warm water; it is now free from benzoic acid and chloride of benzoyl. On boiling the resinous mass with absolute alcohol, a trace of a yellowish secondary product dissolves, leaving the principal quantity undissolved, which then appears as a white crystalline mass.

When the product thus obtained is boiled with a large quantity of ether, and the solution allowed to cool, small crystals are deposited, which are soluble with difficulty in ether. Absolute alcohol dissolves only a trace of this substance, and when boiled with it deposits the dissolved part, on cooling, in minute spherical aggregations of crystals, which under the microscope are seen to be prismatic.

The best solvent for this compound is benzol, it being soluble in all proportions in this liquid. On evaporating the solution, the substance is left behind in fine prismatic crystals. Chloroform behaves like benzol: but the crystals obtained from this solvent are much finer, and can be obtained of considerable size.

In order to ascertain the nature of the compound produced by the action of chloride of benzoyl on sycocerylic alcohol, we decomposed it by means of sodium-alcohol, which we found to be preferable to any other form of caustic alkali. Even with this reagent the decomposition is effected only with difficulty, possibly on account of the new substance being only sparingly soluble, and also on account of the resulting benzoate of sodium not being much more soluble in the alcohol. However, after boiling for some time, the benzoate of sycoceryl disappears. On addition of water, a bulky substance was separated, which proved to be the regenerated alcohol of sycoceryl.

The aqueous liquid saturated with an acid soon formed a crystalline precipitate, which, on removal with ether, proved to be benzoic acid.

The foregoing experiments bear conclusive evidence that the alcohol of sycoceryl behaves towards chloride of benzoyl in a manner perfectly analogous to that of other members of the alcoholic group, producing, that is to say, a benzoate of the ether-radicle.

After having shown that the substance separated by sodium-alcohol may be regarded as the alcohol of the new radicle sycoceryl, it became desirable to have a synthetic proof of this theory; and it occurred to us that if we could succeed in combining the sycocerylic alcohol again with the radicle of acetic acid, and thus reproduce the original substance, which we have called acetate of sycoceryl, it would be the best possible confirmation of our views. In order to test this, we accordingly brought chloride of acetyl in contact with sycocerylic alcohol. At ordinary temperatures, no action took place; but when a little heat was applied the alcohol was dissolved, and the liquid commenced to boil, giving off copious fumes of hydrochloric acid. After the reaction had ceased, heat was again applied, and the whole subjected to the boiling temperature for some time, in order to get rid of the excess of chloride of acetyl. After cooling, the resulting product was boiled with water, when a heavy oily body separated. The boiling with water was continued for some time, until at last the oily liquid became perfectly solid and beautifully crystalline, indicating at once that a substance had been formed differing from the original alcohol, which, it will be remembered, is fluid at the temperature of boiling water.

This white crystalline substance was now dissolved in boiling alcohol, of which it required a considerable quantity, and subsequently allowed to cool. When almost the whole had dissolved, a small quantity of a compound was left behind, which at last melted, being evidently a new substance, the probable product of the action of a small quantity of oxychloride or phosphorus which contaminated the chloride of acetyl.

On cooling, the filtered liquid began to crystallize, yielding beautiful iridescent flat prismatic crystals, which sparkled with the colours of the rainbow in the solution, like chlorate of potash in the act of crystallizing. The crystallized substance produced in this experiment proved to be in every respect identical with the natural acetate of sycoceryl, and thus gave the most direct confirmation to our theoretical views.

Having thus established the nature of the sycocerylic alcohol, it became desirable to produce also the acid which would be homologous with benzoic acid, and would bear to this acid a relation similar to that which palmitic acid bears to the lower members of the series to which it belongs. A small quantity of the alcohol was therefore boiled for about six hours with dilute nitric acid. A feeble reaction was indicated by the slight evolution of nitrous fumes, and after some time the sycocerylic alcohol became of a dark yellow colour, and presented a resinous aspect. After digesting for six hours, the resinous product was removed, washed with water, and dried. This substance was readily soluble in warm alcohol, and on cooling a white crystalline substance was deposited. This crystalline substance had all the characters of an acid; it was perfectly soluble in an aqueous solution of potash or ammonia, and gave with an alcoholic solution of acetate of lead a copious precipitate. Although this reaction showed that we had obtained an acid which possesses all the properties that might be anticipated of an acid corresponding to our alcohol, we could not, with the very small quantity of substance at our disposal, get enough of it in a pure state for analysis, on account of the yellow nitro-compound (apparently the nitro-acid of the new acid) adhering with great obstinacy to it, and accompanying it in all its compounds and solutions. In order to exclude the formation of this secondary product, we tried the action of chromic acid on sycocerylic alcohol; a small quantity of the alcohol was boiled with a moderately concentrated solution of chromic acid for about eight hours. The product so obtained was washed and boiled with a dilute solution of potash, but after saturating this alkaline solution with an acid, no precipitate was formed, and it was altogether impossible to detect any acid: therefore we must conclude that this acid was not formed by this treatment.

On one occasion, on repeating this experiment, we accidentally observed, among the products of the action of chromic acid on sycocerylic alcohol, a crystalline body; on treating the mass with dilute alcohol, this product was procured in large flat prisms, resembling somewhat in appearance the acetate of sycoceryl, but differing in its melting-point, and was perfectly neutral. From the mode of formation, it might be inferred that we had obtained the aldehyde ($C_{18}H_{28}O$) corresponding to our alcohol, but the minuteness of the quantity procured rendered it impossible to decide this point.

For the present we must content ourselves with the foregoing account of the compounds of the radicle sycoceryl, the very small amount of the substance at our disposal being barely sufficient for the performance of those experiments which we have described.

The great interest which naturally attaches to this new homologue of the benzyl-alcohol series will be a sufficient inducement for us to take up this subject again, for the purpose of studying its derivatives, should we be so fortunate as to obtain a further supply of raw material.

On reviewing the members of which Cannizzaro's benzylic alcohol is the type, and with which our new alcohol must be classed, it will be perceived that there are still many gaps to be filled up in their series.

Benzylic alcohol	C_7H_8O	
	$C_8H_{10}O$	unknown.
	$C_9H_{12}O$	
Cuminylic alcohol (Thymol and Carvacrol).	$C_{10}H_{14}O$	
	$C_{11}H_{16}O$	unknown.
	$C_{12}H_{18}O$	
	$C_{13}H_{20}O$	
	$C_{14}H_{22}O$	
	$C_{15}H_{24}O$	
	$C_{16}H_{26}O$	
	$C_{17}H_{28}O$	
Sycocerylic alcohol	$C_{18}H_{30}O$	

On comparing the properties of our sycocerylic alcohol with those of benzylic alcohol, very little resemblance will at first be traceable between them; but when it is remembered that there are not fewer than ten steps between benzylic and sycocerylic alcohol, this difference of properties is easily accounted for; more particularly if we take into consideration a similar case in another homologous series, the links of which are more fully known. The change in the properties of the acetic acid series, for example, by each increment of increase of CH_2, is quite as remarkable; and when we compare acetic acid on the one hand, with palmitic acid on the other, the dissimilarity is not less remarkable than if we compare sycocerylic alcohol, $C_{18} H_{30} O$, with benzylic alcohol, $C_7 H_8 O$.

In conclusion, we may mention that benzylic alcohol, and consequently also cuminylic alcohol, are generally considered to be homologues of phenyl-alcohol (carbolic acid); cresyl-alcohol would be isomeric with benzyl-alcohol, and carvacrol and thymol with cuminylic alcohol. On comparing these substances, we find that this view is not tenable, and that there exist in reality at least two distinct series of isomeric compounds, the types of which are benzylic alcohol on the one hand and phenylic alcohol on the other.

The crystalline substance which adhered to the acetate of sycoceryl, and which it will be recollected was left in part undissolved when the acetate was dissolved out with ether, can be obtained in only very small crystals. It is perfectly neutral, and we did not succeed in obtaining any derivative from it calculated to throw light on its true nature. The quantity was indeed extremely small, and we therefore content ourselves with giving the results of the ultimate analysis of this substance, which was found to contain 75·56 per cent. carbon and 12·30 per cent. hydrogen.

XV.—*On a Deposit of Crystallized Xanthin in Human Urine.*

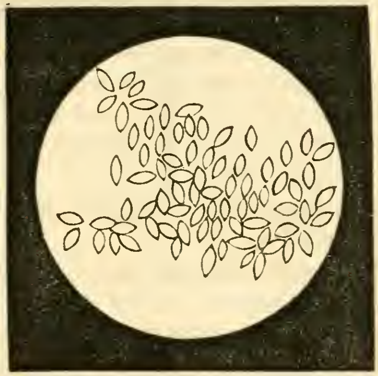
By H. Bence Jones, M.D., F.R.S.

In July, 1861, I was consulted regarding a schoolboy, nine years and a half of age. The following history was given to me. He had good health until seven years old, when he was seized one night with violent sickness and pain in the stomach, which continued incessantly for three days. Neither mustard poultices, blisters, nor leeches relieved the pain or stopped the sickness. The third day his water gradually became of the colour of blood; it then stopped altogether, and nothing was passed for four days; then delirium and convulsions came on, and these lasted for twenty-four hours, when he was relieved by a most violent perspiration. No stone was seen to pass. In a few days he was perfectly well, and continued so for nearly three years, when in

June, 1861, he caught a slight cold, and was delirious one night. A medical man saw him and found some albumen in the urine, which then was generally thick, and the quantity of deposit was increased by excitement, or temper; cold produced the same effect in a less degree. He never complained of pain in the back, and was able to take more exercise than other boys of his age without fatigue. He always had a good appetite, and was allowed to eat everything.

On examination I found a very small quantity of albumen in the water made at night, and none in that made in the morning. There were no blood cells, no tubular casts, and the specific gravity was high. I examined many specimens without finding anything remarkable.

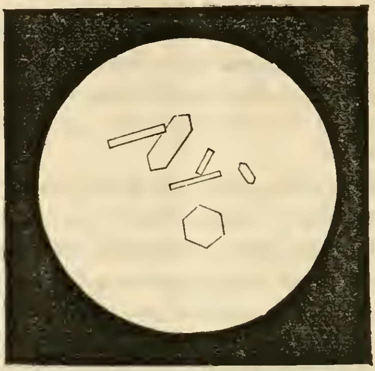
About the end of July, when he was leaving London, a small vial of urine was sent to me, which was quite thick and deep-coloured. A drop was placed under the microscope, and a crystalline deposit was found resembling one form of uric acid. From the form I considered the deposit was uric acid.



On examining the unfiltered urine for albumen by heat, I was surprised to see the crystalline deposit entirely dissolve. A fresh portion of sediment showed the same crystalline appearance and the same solubility by heat. This was so utterly unlike any uric acid deposit, that a closer examination of the sediment was made, but so little substance was left that no satisfactory conclusion could be arrived at, except that it was not uric acid.

A day or two afterwards another specimen was brought to me containing the same crystalline deposit soluble by heat. The sediment formed about an eighth of the bulk of the fluid. It was collected on a filter, washed with alcohol, and it gave the following reactions. It dissolved in water and in hydrochloric acid; when treated with nitric acid, it dissolved without effervescence, and when evaporated to dryness, it left a yellow residue.

When the solution in hydrochloric acid was evaporated to dryness it left beautiful minute crystals of this form:—



These crystals were soluble in water.

The sediment was easily dissolved by alkalies.

The watery solution of the sediment had a feebly acid reaction, and when evaporated to dryness, left an amorphous residue, which was again easily dissolved in water.

These reactions agree only with the latest and best observations of the reactions of xanthin.

Hoping to get more of the substance, I wrote to the country for the sediment of the urine. It was collected on many occasions, but I could only find urates and uric acid, and none of the crystalline deposit soluble by heat.

In January, 1862, the same boy was brought to me, with two specimens of urine and four different dried deposits; and at different times for three weeks I examined the urine. It was generally of high specific gravity, 1025, 1026, 1027, 1030; once as low as 1013. It sometimes contained a trace of albumen. Usually it contained urates, and sometimes uric acid and oxalate of lime, but never the crystalline deposit soluble by heat.

The dried deposits consisted of urates and uric acid, and one of them consisted of phosphate of lime, with a little phosphate of ammonia and magnesia, without a trace of uric acid or xanthin.

XVI.—*On the Simultaneous Variations of Hippuric and Uric Acids in Healthy Urine.*

By H. Bence Jones, M.D., F.R.S.

In *Henle's Zeitschrift für rationelle Medicin,* 1858, ii., 331, Dr. A. Weismann gives the results of his experiments on the amount of hippuric acid in healthy urine These results were obtained by evaporating very small quantities (20 cc.) of urine, and they show so large an amount of hippuric acid excreted daily, that a different method of analysis seemed most desirable. The average amount excreted during four days of mixed diet he gives as 40·6 grs. daily.

M. Wreden, in the *Bulletin de St. Petersburg, Classe Phys.-med.* xvii., 500, states that he determined the amount of hippuric acid in healthy urine by means of a standard solution of chloride of iron; the amount he obtained was also immense.

He gives, as the mean of twenty-nine determinations, 47·4 grs. of hippuric acid to a litre (1000 cc.) of urine = 1·7 pint. The minimum amount found was 32·3 grs., and the maximum 87·8 grs. to a litre.

In the following experiments, the method of determining hippuric acid, described by Professor Liebig, in the *Annalen der Chemie und Pharmacie,* vol. 50, p. 170, was followed, as being the most accurate, provided a sufficient quantity of urine is taken for analysis and sufficient ether is used. Usually 400 cc. of urine were evaporated to a syrupy consistence in a water-bath; hydrochloric acid was added, and the hippuric acid was extracted by treating the precipitate with ether four or five times. That by this method results are obtained which agree very well together, the following experiments show:

840 cc. of urine were divided into two equal parts, and the amount of hippuric acid in each part was determined.

Weight of hippuric acid, 1st experiment, 3·53 grs.; 2nd experiment, 3·42 grs.

700 cc. were divided into two equal parts and the hippuric acid was determined in each.

Weight of hippuric acid, 1st experiment, 1·49 gr.; 2nd experiment, 1·42 gr.

The determination of the amount of uric acid in all the following experiments (except in experiments 13, 14, 15, 16), was made after the hippuric acid had been extracted by ether. The syrupy residue was then diluted with a little water, and filtered 24 hours afterwards. The uric acid was dissolved in soda, precipitated by hydrochloric acid, and collected 24 hours afterwards.

In experiments 13, 14, 15, and 16, a separate quantity of urine was taken, to which hydrochloric acid was added, and after standing 24 hours, the uric acid was collected on a filter.

Two healthy men were the subjects of the experiments.

The diet of A, who weighed 10st. 12lbs., was, breakfast (8½ a.m.) tea, bread and butter; luncheon (1 p.m.) bread and butter; dinner (5½ p.m.) a pound and a-half of meat, bread and tea; supper (9 p.m.) bread and cheese, and pint of beer. Moderate exercise was taken.

The diet of B, weighing 14st. 6lbs., was, breakfast (9 a.m.) about ⅔ pound of meat, bread, butter, and tea; dinner (7 p.m.) about one pound of meat and some vegetables, with brandy and water or tea. Very little exercise was taken.

Firstly, experiments were made on the total quantity of hippuric acid excreted in 24 hours.

A. The total amount of urine passed in 24 hours was 930 cc.; sp. gr. 1022. 400 cc. were taken for the determination of the hippuric acid. The uric acid was lost by accident.

Weight of hippuric acid 2·64 grs. Hence 930 cc. contained hippuric acid 6·1 grs.

A. The total amount of urine passed in 24 hours was 980 cc.; sp. gr. 1020. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid, 1·68 gr.; weight of the uric acid, 3·44 grs. Hence the 980 cc. contain hippuric acid 4·1 grs.; uric acid 8·4 grs.

A. The total amount of urine passed in 24 hours was 790 cc.; sp. gr. 1022.

Weight of hippuric acid 2·42 grs.; weight of uric acid 3·60 grs. Hence the 790 cc. contain hippuric acid 4·7 grs.; uric acid 7·1 grs.

Hence the daily excretion of A in the three experiments was:

	1st.	2nd.	3rd.	Mean.
Hippuric acid .	6·1 grs.	4·1 grs.	4·7 grs.	4·9 grs.
Uric acid . .	—	8·4 grs.	7·1 grs.	7·7 grs.

B. The total amount of urine passed by B in 24 hours was 1460 cc.; sp. gr. 1017. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid 2·00 grs.; weight of uric acid 4·00 grs. Hence the 1460 cc. contain hippuric acid 7·3 grs.; uric acid 14·6 grs.

B. The total amount of urine passed in 24 hours was 1103 cc.; sp. gr. 1019.

Weight of hippuric acid, 1st experiment, 2·00 grs.; 2nd experiment, 2·12 grs. Weight of uric acid, 1st experiment, 3·95 grs.; 2nd experiment, 4·00 grs.

Hence the 1103 cc. contain—

	1st exp.	2nd exp.	Mean.
Hippuric acid	5·5 grs.	5·8 grs.	5·65 grs.
Uric acid	10·8 grs.	11·0 grs.	10·9 grs.

B. The total amount of urine passed in 24 hours was 1510 cc.; sp. gr. 1017. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid, 1st experiment, 1·98 gr.; 2nd experiment, 2·08 grs. Weight of uric acid, 1st experiment, 3·46 grs.; 2nd experiment, 3·54 grs. Hence the 1510 cc. contain—

	1st exp.	2nd exp.	Mean.
Hippuric acid	7·45 grs.	7·8 grs.	7·6 grs.
Uric acid	13·0 grs.	13·3 grs.	13·1 grs.

B. The total amount of urine passed in 24 hours was 1326 cc.; sp. gr. 1019. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid 1·76 gr.; weight of uric acid 3·80 grs. Hence the 1326 cc. contain hippuric acid 5·8 grs.; uric acid 12·5 grs.

Hence the daily excretion of B in the four experiments was—

	1st.	2nd.	3rd.	4th.	Mean.
Hippuric acid	7·3 grs.	5·6 grs.	7·6 grs.	5·8 grs.	6·5 grs.
Uric acid	14·6 grs.	10·9 grs.	13·1 grs.	12·5 grs.	12·6 grs.

Secondly, to determine the variations in the amount of hippuric and uric acids in the urine, passed before and after food, a long series of experiments were made with the urine of B.

In the following four experiments 400 cc. of urine passed before and after food were taken:

Experiment 1.—Before food, sp. gr. 1016; weight of hippuric acid 1·52 gr.; weight of uric acid 2·70 grs. After food, sp. gr. 1018; weight of hippuric acid 2·70 grs.; weight of uric acid 4·64 grs.

Experiment 2.—Before food, sp. gr. 1013; weight of hippuric acid 1·10 gr.; weight of uric acid, 2·80 grs. After food, sp. gr. 1019; weight of hippuric acid 1·94 gr.; weight of uric acid 4·78 grs.

Experiment 3.—Before food, sp. gr. 1016; weight of hippuric acid 1·12 gr.; weight of uric acid 3·46 grs. After food, sp. gr. 1019; weight of hippuric acid 3·88 grs.; weight of uric acid 5·32 grs.

Experiment 4.—Before food, sp. gr. 1013; weight of hippuric acid 1·34 gr.; weight of uric acid 1·92 gr. After food, sp. gr. 1018; weight of hippuric acid 3·60 grs.; weight of uric acid 3·00 grs.

In the next six experiments 350 cc. of urine were taken:

Experiment 5.—Before food, sp. gr. 1014; weight of hippuric acid 1·46 gr.; weight of uric acid 2·62 grs. After food, sp. gr. 1016; weight of hippuric acid 1·94 grs.; weight of uric acid 3·80 grs.

Experiment 6.—Before food, sp. gr. 1012; weight of hippuric acid 2·02 grs.; weight of uric acid 0·68 gr. After food, sp. gr. 1012; weight of hippuric acid 1·20 gr.; weight of uric acid 2·04 grs.

Experiment 7.—Before food, sp. gr. 1019; weight of hippuric acid 2·04 grs.; weight of uric acid 3·43 grs. After food, sp. gr. 1014; weight of hippuric acid 2·84 grs.; weight of uric acid 2·84 grs.

Experiment 8.—Before food, sp. gr. 1012; weight of hippuric acid 1·12 gr.; weight of uric acid 1·14 gr. After food, sp. gr. 1013; weight of hippuric acid 1·62 gr.; weight of uric acid 2·24 grs.

Experiment 9.—Before food, sp. gr. 1019; weight of hippuric acid 1·44 gr.; weight of uric acid 1·90 gr. After food, sp. gr. 1·017; weight of hippuric acid 1·97 gr.; weight of uric acid 2·30 grs.

Experiment 10.—Before food, sp. gr. 1012; weight of hippuric acid 1·01 gr.; weight of uric acid 0·10 gr. After food, sp. gr. 1016; weight of hippuric acid 1·01 gr.; weight of uric acid 1·88 gr.

Experiment 11.—375 cc. of urine passed before and after food were taken. Before food, sp. gr. 1020; weight of hippuric acid 1·41 gr.; weight of uric acid 2·92 grs. After food, sp. gr. 1016: weight of hippuric acid 1·18 gr.; weight of uric acid 2·94 grs.

Experiment 12.—Before food, sp. gr. 1022; weight of hippuric acid 1·36 gr.; weight of uric acid 2·56 grs. After food, sp. gr. 1025; weight of hippuric acid 1·94 gr.; weight of uric acid 4·92 grs.

Experiment 13.—570 cc. of urine passed before and after food were taken for the determination of the hippuric acid; and 190 cc. of urine passed before and after food were taken for the determination of the uric acid. Before food, sp. gr. 1014; weight of hippuric acid 1·20 gr.; weight of uric acid in 190 cc. 0·61 gr.; ditto, in 570 cc. 1·83 gr. After food, sp. gr. 1015; weight of hippuric acid 2·02 grs.: weight of uric acid in 190 cc. 1·32 gr.; ditto, in 570 cc. 3·96 grs.

Experiment 14.—380 cc. of urine passed before food were taken for the determination of the hippuric acid, and 240 cc. for uric acid. 380 cc. of urine passed after food were taken for the determination of both. Before food, weight of hippuric acid 3·80 grs.; weight of uric acid in 240 cc. 2·26 grs; ditto, in 380 cc. 3·50 grs. After food, weight of hippuric acid 2·26 grs.; weight of uric acid in 380 cc. 4·60 grs.

Experiment 15.—300 cc. of urine passed before food were taken for the determination of the hippuric acid, and 200 cc. for uric acid; 300 cc. of urine passed after food were taken for the determination of both. Before food, weight of hippuric acid 2·00 grs.; weight of uric acid in 200 cc. 1·20 gr.; ditto, in 300 cc. 1·80 gr. After food, weight of hippuric acid 1·18 gr.; weight of uric acid in 300 cc. 2·30 grs.

Experiment 16.—127 cc. of urine were taken before food for the determination of the hippuric and uric acids, and 150 cc. of urine were taken after food for the determination of the hippuric and uric acids. Before food, weight of hippuric acid in 127 cc. 1·01 gr.; weight of uric acid in 127 cc. 1·24 gr. After food, weight of hippuric acid in 150 cc. 1·10 gr.; ditto, in 127 cc., 0·93 gr.; weight of uric acid in 150 cc. 1·68 gr.; ditto, 127 cc., 1·42 gr.

Experiment 17.—400 cc. of urine were taken before food for the determination of the hippuric and uric acids, and 244 cc. of urine were taken after food for the determination of the hippuric and uric acids. Before food, sp. gr. 1013; weight of hippuric acid in 400 cc. 1·80 gr.; weight of uric acid in 400 cc. 2·54 grs. After food, sp. gr. 1023; weight of hippuric acid in 244 cc. 3·00 grs.; ditto, in 400 cc. 4·90 grs.; weight of uric acid in 244 cc. 3·78 grs.; ditto, in 400 cc., 6·19 grs.

Hence, there were in 1000 cc. of urine before food, and in 1000 cc. of urine after food,—

	Before Food.				After Food.		
Exp.		Sp. Gr.	Grs.		Sp. Gr.	Grs.	
1.	Hippuric acid	1016	3·8	..	1018	6·7	hippuric acid
	Uric ,,	,,	6·8	..	,,	11·6	uric ,,
2.	Hippuric ,,	1013	2·7	..	1019	4·8	hippuric ,,
	Uric ,,	,,	7·0	..	,,	11·9	uric ,,
3.	Hippuric ,,	1016	2·8	..	1019	9·7	hippuric ,,
	Uric ,,	,,	8·6	..	,,	13·3	uric ,,
4.	Hippuric ,,	1013	3·3	..	1018	9·0	hippuric ,,
	Uric ,,	,,	4·8	..	,,	7·5	uric ,,
5.	Hippuric ,,	1014	4·1	..	1016	5·5	hippuric ,,
	Uric ,,	,,	7·4	..	,,	10·8	uric ,,
6.	Hippuric ,,	1012	5·7	..	1012	3·4	hippuric ,,
	Uric ,,	,,	1·9	..	,,	5·7	uric ,,
7.	Hippuric ,,	1019	5·8	..	1014	8·1	hippuric ,,
	Uric ,,	,,	9·8	..	,,	8·1	uric ,,
8.	Hippuric ,,	1012	3·2	..	1013	4·5	hippuric ,,
	Uric ,,	,,	3·2	..	,,	6·4	uric ,,
9.	Hippuric ,,	1019	4·1	..	1017	5·6	hippuric ,,
	Uric ,,	,,	4·2	..	,,	6·5	uric ,,
10.	Hippuric ,,	1012	2·8	..	1016	2·8	hippuric ,,
	Uric ,,	,,	0·2	..	,,	5·3	uric ,,
11.	Hippuric ,,	1020	3·7	..	1016	3·1	hippuric ,,
	Uric ,,	,,	7·7	..	,,	7·8	uric ,,
12.	Hippuric ,,	1022	3·6	..	1025	5·1	hippuric ,,
	Uric ,,	,,	6·8	..	,,	13·1	uric ,,
13.	Hippuric ,,	1014	2·1	..	1015	3·5	hippuric ,,
	Uric ,,	,,	3·2	..	,,	6·9	uric ,,
14.	Hippuric ,,	,,	10·0	..	,,	5·9	hippuric ,,
	Uric ,,	,,	9·4	..	,,	12·1	uric ,,
15.	Hippuric ,,	,,	6·6	..	,,	3·9	hippuric ,,
	Uric ,,	,,	6·0	..	,,	7·6	uric ,,
16.	Hippuric ,,	,,	7·9	..	,,	7·3	hippuric ,,
	Uric ,,	,,	9·7	..	,,	11·2	uric ,,
17.	Hippuric ,,	1013	4·5	..	1023	12·2	hippuric ,,
	Uric ,,	,,	6·3	..	,,	15·4	uric ,,

Hence the average, in 1000 cc. of urine before food, is—sp. gr. of urine 1015·3—hippuric acid 4·51 grs; uric acid 6·05 grs. After food, sp. gr. 1017·2; hippuric acid 5·94 grs.; uric acid 9·48 grs.

It follows, from these two series of experiments on the quantity of hippuric and uric acid excreted in twenty-four hours, and on the increase or diminution of the hippuric and uric acids in the urine after food, that in 24 hours:—

1. The lighter man gave 4·96 grs. of hippuric acid
and 4·74 grs. of uric acid;
the mean quantity of urine being 1·25 pints.

The heavier man gave 6·5 grs. of hippuric acid
and 11·6 grs. of uric acid;
the mean quantity of urine being 2·37 pints.

2. The hippuric acid was increased, on an average, in the heavier man
from 4·51 grs. per 1000 cc. urine before food
to 5·94 grs. ,, ,, after food

Whilst the uric acid was increased on an average
from 6·05 grs. ,, ,, before food
to 9·45 grs. ,, ,, after food

Liebig states,* that all the urine that he examined of persons living on mixed diet contained about equal quantities of hippuric and uric acid.

Parkes, in his work, "On the Composition of the Urine," p. 12, gives the amount of uric acid found by fourteen observers in the urine secreted in 24 hours. The lowest quantity was 4·32 grs., and the highest 14·49 grs. The mean of all the observations together was 8·5 grs. of uric acid in 24 hours.

As yet I have made only a very few experiments on the amount of hippuric acid present in the urine in diseased states of the body.

Bouchardat, in the "Annuaire de Thérapeutique" for 1842, p. 285, speaks of a disease which he calls "hippurie." A case resembling his description was met with in St. George's Hospital. The urine was very dilute, of yellowish colour, and feebly alkaline reaction. 420 cc. of urine contained only traces of hippuric acid.

In a case of acute rheumatic fever, the sp. gr. of the urine was

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* Ann. Ch. Pharm. 50, p. 170.

1010; it had a brown yellow colour and acid reaction. 350 cc. of this urine contained a very small quantity of hippuric acid.

In a case of diabetes (sp. gr. of the urine 1040), 400 cc. of urine were examined for hippuric acid, but only traces were found.

These experiments only show that a far more extended inquiry is requisite to find the variations of hippuric acid in disease.

In conclusion, I must express my obligation to Dr. Ulrich for the care he took to make these results as accurate as possible.

XVII.—*On Ground Ice.*

By Richard Adie, Liverpool.

In a note to the paper on this subject which I last year submitted to the Chemical Society, Dr. Frankland has referred to the phenomenon of ground ice, as well known to take place in rapidly flowing streams, and as having for its origin a source which I imagine to be similar to that adduced by M. Arago, in his paper on this question in the "Annuaire" for 1833, namely, "the aptitude to the formation of crystals of ice on stones and asperities of the bottom cooled to 32° F."

I wish to return to the subject to state that the district where ground ice is to be found very much more frequently than in any other place with which I am acquainted, is called "Altcar," about 11 miles north of Liverpool. Here I have found it twice during two moderate frosts of the present month of January, 1862. The country there is flat, with wide, slow-flowing ditches separating the fields, and no hedge-rows or fences. Here two nights' moderate frost appear to be sufficient to cool down the water on the surface of these ditches to near 32° F. When this occurs, there is a supply of ice-crystals, derived chiefly from a fringe of them along the edges, which are seen to be continually detached and floated down with the current. Now, it is to these crystals that I attribute the lodgments of ice: for they are found in the places most suited to their detention, without any reference to the exposure of the surface—for example, where a stream sweeps round a turn or corner, the weeds or plants there are sure to be the first to contain submerged ice.

On the surface there is a supply of asperities for the formation of crystals at the edges more than at any other part of the stream; and, as the temperature is often ten degrees lower at the surface than it can be under water, this view of the question is in accordance with all the observed facts.

On the 1st of January, I examined a stream, locally known by the name of "The Brook," a tributary of the river Alt, and found ice on the plants in the bed of the stream at places favourable to its detention; some of it had a soiled aspect, and contained many air-bubbles, giving evidence of two or three days age. The frost was of a mild character, but of several days' duration. Surface ice on stagnant pools was trustworthy to walk on only where the water was shallow.

On the 22nd of January I again visited the Altcar district, after a second frost of a few days' duration had been established. At this time, the thermometer had ranged six to eight degrees below 32° on the Fahrenheit scale, accompanied by a brisk, piercing wind. There was abundance of ground ice in the tributary, and also in the river Alt, where I had not before found it. In some parts, where on former occasions ground ice had been plentiful, at the present time surface ice covered everything; but it showed that, while forming, it had received large supplies of the ground ice. This I particularly remarked around and under the arch of a narrow bridge, where a quantity of spherical-shaped masses, such as collect on the plants that twist and turn in the bed of a stream, had been floated into a mass stretching across the surface, and there frozen into strong ice.

I remember having seen a remark that in some districts ground ice is a characteristic of the beginning of a frost, of which the above observation gives a confirmation; and I have no doubt that a quick, sharp frost would cover the waters in Altcar with surface ice, to the exclusion of the formation of ground ice, but I have not been in the neighbourhood on such an occasion to examine them.

The early period of the winter at which it has been recorded that ground ice was abundant, is another proof that it belongs to the beginning of a frost. A friend of mine wrote from Hawick, under date 17th November, 1841, that he had seen ground ice in abundance in the river Teviot. This fact of ground ice making its appearance at the early part of a frost, strongly favours the view that it is derived from edge-formed crystals: for this is the place where on every occasion the ice will first form.

Dr. Farquharson, who described the ground ice in the ditches of Lincolnshire, in the "Transactions of the Royal Society," appears to have had a district as favourable for showing it as Altcar.

The reason why streams of a flat country are so much more quickly cooled to near the freezing point than those of a more uneven surface is, that they are free from underground supply, either from natural or artificial sources. I can remember examining a slow-flowing stream which received the water of many tile drains; this, during a severe frost, ran in the centre as clear as in a midsummer day, with only a light fringe of ice crystals along the edges.

In the valley of the Tay, and some of the northern rivers of the island, the people resident say that a frozen fog is a freqent precursor of ground ice. While examining the Altcar ground on the 1st of January, I had a palpable proof of the immense quantity of ice-crystals a wooded district would supply to a stream running underneath the branches of the trees. The weather at the close of the year was foggy, the night frosts covering wooded districts with beautiful displays of ice-foliage. For two or three successive days, the sun's rays had power so far to relax the frost that the ice fell from the branches to the frozen ground. When on the ground the ice did not melt much. The branches were thus daily prepared to receive a fresh supply from the frosty and foggy night air. In this manner a large quantity of ice-crystals had collected in the shade of every tree, and these, be it observed, were more available for ground ice in a stream than if they had been supplied by snow, for in the latter case the surrounding country is covered, and the streams receive water as if from drains.

Some years ago, when I first examined ice in the beds of streams, I held the opinion that the temperature of 32° was indispensable for its appearance and preservation. From more recent experiments, I am of opinion that the ground ice may be preserved and be lodged with the water of the stream from three to five-tenths of a degree of Fahrenheit above the freezing point, when the temperature of the external atmosphere is low enough to form ice-crystals at the surface along the edges.

XVIII.—*On the occurrence of considerable Deposits of Crystallized Phosphate of Lime in Teak-wood.*

By F. A. Abel, F.R.S.

The wood of the *Tectona grandis,* which is imported from the south of India and a few other tropical countries, has been very extensively employed within the last few years in connexion with military equipments (for example, in the construction of gun-carriages, packing cases, &c.), required for use in tropical climates, as it is greatly superior to other descriptions of wood in its power of resisting the destructive effects of extreme changes of temperature.

In the reduction of the large blocks of teak-wood to planks and small timber, deposits of a white substance, sometimes soft and pulverulent, at other times so hard as quickly to blunt the cutting edges of the saws employed, are constantly met with, intersecting the wood in the form of layers converging towards the centre or heart of the tree, from which point they usually start. These layers or deposits are often several feet in length (some have been found to extend more than six feet), and measure six or eight inches in breadth, the thickness of the layers varying from one-eighth to three-eighths of an inch. Where these layers occur, they have evidently been gradually deposited in flaws or cracks (so called shakes), which have formed in the living tree. Cavities, occasioned by knots in the wood are frequently lined or filled with the same white deposit; as are also the perforations, of considerable size and length, which are constantly met with in the teak-wood, and which owe their existence to the labours of a large caterpillar. The remains of huge moths into which these insects have become transformed, are occasionally found in the wood; the bodies of these consist of a ceraceous substance, which on examination was found to exhibit the general properties of the product of the long-continued action of moisture upon fatty matters, known as adipocere.

The white deposit, the occurrence of which has just been described, exhibits occasionally a very distinct striated crystalline structure, and sometimes consists of conglomerates of small acicular crystals, easily distinguished by the aid of a microscope of low power. It is readily soluble in dilute acids, with separation of a very small quantity of organic colouring matter. Effervescence is not generally observable on dissolving the substance, but on the application of a very gentle heat to the solution, a minute quantity of carbonic acid gas is disengaged.

The analysis of an average specimen of this deposit, dried in *vacuo*, yielded the following per-centage results:—

Lime	34·04	per cent.
Magnesia	1·86	,,
Ammonia	1·12	,,
Phosphoric acid . . .	43·35	,,
Carbonic acid . . .	trace	
Water, and a minute proportion of organic matter	19·54	,,

From the relations which the small proportions of magnesia and ammonia, included in the above results, bear to each other, they evidently exist in the substance in the form of ordinary ammonio-phosphate of magnesia, $2MgO \, . \, NH_4O \, . \, PO_5 + 12 \, Aq$:— 1·86 per cent. of magnesia in this form would require 1·20 per cent. of ammonia; the per-centage obtained was 1·12. By calculating from the per-centage of magnesia, the proportion of the above double-salt existing in admixture with the phosphate of lime, the following numbers are obtained:—

Magnesia	1·86	per cent.
Ammonia	1·20	,,
Phosphoric acid . .	3·35	,,
Water	5·02	,,

The amount of ammonio-phosphate of magnesia present in the specimen analysed would, therefore, be 11·43 per cent. Deducting the above numbers from the analytical results obtained, the following proportions of phosphoric acid, lime, and water remain:—

Lime	34·04
Phosphoric acid	40·00
Water	14·52

which, calculated upon one hundred parts, yield the following numbers:—

Lime	38·44
Phosphoric acid	45·17
Water	16·39
	100·00

The proportions which the acid and base bear to each other in these numbers, admit the conclusion that the form in which they are combined is in the proportion of two equivalents of lime to one of phosphoric acid, the lime being about three per cent. in excess of the amount required to form a salt containing two equivalents of the base, while it is more than twelve per cent. below what would be required to form a tri-phosphate.

I was at first disposed to regard this phosphate of lime, which, as above stated, frequently exists in the form of distinct crystals, as the crystallized di-phosphate, which may be produced by adding lime-water to the acid phosphate of lime, $CaO . 2HO . PO_5$, by dissolving lime in a slight excess of phosphoric acid, or by digesting the amorphous tri-phosphate of lime with a proportion of an acid, such as hydrochloric acid, insufficient for its solution. But the composition of this salt, which Bödeker describes as containing four equivalents of water of crystallization ($2 CaO . HO . PO_5 + 4 Aq.$) does not accord with the numbers obtained.* On comparing them, however, with the per-centage proportions required for a di-phosphate of lime of the formula $2 CaO . HO . PO_5 + 2 Aq.$, containing, therefore, two equivalents less of water of crystallization than the salt described by Bödeker, they correspond pretty closely, particularly when it is remembered that a small proportion of the lime discovered in the deposit existed in the form of carbonate.

The following is a comparison of the per-centage results with the numbers demanded by the above formula, $2 CaO . HO . PO_5 + 2 Aq.$:—

2 CaO	56	36·13	38·44
PO_5	72	46·45	45·17
3 HO	27	17·42	16·39
	155	100·00	

It is, however, also not improbable that the deposits of phosphate of lime which have been described, and which vary considerably in the degree of crystalline structure exhibited, may consist of variable mixtures of amorphous and crystallized di-phosphate of lime.

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* In Gmelin's Handbook, vol. iii. p. 195, the theoretical numbers given for comparison with the results of Bödeker's analysis of this salt are calculated upon *four* instead of *five* equivalents of water; hence the results of that chemist do not appear to agree well with the formula given, whereas they accord closely with those demanded by the formula $2 CaO. HO. PO_5 + 4 Aq.$

XIX.—*On the Chemical Constitution and Artificial Formation of Taurine.*

By HERMANN KOLBE, of Marburg.

SOME years ago, Strecker* made the interesting observation that isethionate of ammonia, when heated to 210° C., gives off water, and is converted into taurine. By this discovery, as well as by the more recent observation of Gibbs,† that taurine treated with nitrous acid is reconverted into isethionic acid, the existence of intimate relations between taurine and isethionic acid was placed beyond doubt; but the question relating to the chemical constitution of taurine, with which that of isethionic acid is closely connected, still remained undecided. That taurine is not the amide of isethionic acid, is sufficiently shown by its behaviour with hydrate of potash, which does not eliminate ammonia from it till heated to the melting point, and then completely decomposes it.

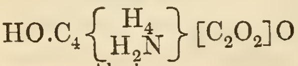
I believe that I have found the key to the solution of this problem, by an experimental confirmation of the conjecture which I threw out a short time ago,‡ that taurine is related to isethionic acid in the same manner as alanine to lactic acid. In the same sense that the two last-mentioned bodies may be regarded as derivatives of ethyl-carbonic (propionic) acid, that is to say, alanine as amido-ethyl-carbonic acid, and lactic acid as oxy-ethyl-carbonic acid,—so likewise may taurine and isethionic acid be viewed as derivatives of ethyl-sulphuric acid, namely taurine as amido-ethyl-sulphuric acid, and isethionic acid as oxy-ethyl-sulphuric acid: these relations are exhibited by the following formulæ:

$$HO.C_4H_5[C_2O_2]O$$

Propionic acid.

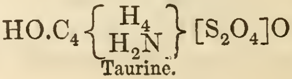
$$HO.C_4H_5[S_2O_4]O$$

Ethyl-sulphuric acid.



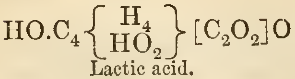
$$HO.C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}[C_2O_2]O$$

Alanine.



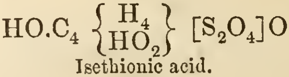
$$HO.C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}[S_2O_4]O$$

Taurine.



$$HO.C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}[C_2O_2]O$$

Lactic acid.



$$HO.C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}[S_2O_4]O$$

Isethionic acid.

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* Ann. Ch. Pharm. xci, 101.

† Jahresbericht der Chemie, xi, 550.

‡ Ann. Ch. Pharm. cxii, 241.

To the assumption that taurine and alanine are so nearly related to each other as these formulæ indicate, it may be objected that taurine does not possess the power which is common to glycocine, alanine, leucine, aspartic acid, amidobenzoic acid, and amido-acids in general, of forming saline compounds both with bases and with acids. But independently of the fact that the organic derivatives of sulphuric acid differ in many points from those of carbonic acid, the following consideration is of especial importance in connection with the present inquiry.

It must, in the first place, be presumed that, by the introduction of amidogen into the ethyl-molecule, the acid properties of ethyl-sulphuric acid will be weakened in the same degree as in alanine, the body derived in like manner from ethyl-carbonic (propionic) acid. But inasmuch as ethyl-sulphuric acid is a stronger acid than propionic acid, it is not surprising that even the weak basic properties of amidated propionic acid should be wanting in the amidated ethyl-sulphuric acid.* On the other hand, this latter acid might be expected to exhibit properties which have not hitherto been actually observed in taurine. Guided by these considerations, I have made several experiments with pure taurine prepared from ox-bile, the results of which I will here briefly communicate.

Taurine dissolved in fuming hydrochloric or strong nitric acid, crystallizes unaltered from the solution on evaporation; moreover, it does not increase in weight when exposed to an atmosphere of dry hydrochloric acid gas, either at ordinary temperatures or when heated. In order to determine whether taurine, like alanine, is capable of forming crystalline compounds with salts, I mixed the concentrated aqueous solutions of equivalent quantities of taurine and chloride of potassium, and abandoned the solution to spontaneous evaporation: pure taurine then crystallized out first, and afterwards chloride of potassium. Neither does the hydrochloric acid solution of taurine yield any compound with bichloride of platinum, alcohol added to the solution producing a precipitate of pure taurine.

It appears therefore that taurine does not exhibit the basic properties possessed by other amido-acids; but, on the other hand, it is by no means destitute of the power of uniting with bases; and, although I have not succeeded in preparing salts of taurine in the solid form, the following experiments show that it is really capable of forming such compounds.

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* Methyl-sulphuric acid, the analogue of acetic acid, does not yield marsh-gas when treated with soda-lime; neither does benzyl-sulphuric acid, the analogue of benzoic acid, yield benzole when thus treated. Other examples of these differences of character are afforded by the observations lately communicated by Vogt (Ann. Ch. Pharm. cxix, 143), and Keller (*ibid.* 153).

A saturated aqueous solution of taurine, in which absolute alcohol immediately produces a copious precipitate, is not precipitated, or even clouded, by a mixture of absolute alcohol and ammonia; but if the solution be then exposed to the air till the ammonia is volatilized, the taurine separates in beautiful crystals. Neither is a concentrated aqueous solution of taurine containing free potash, precipitated by absolute alcohol—a property which may be successfully applied to the separation of taurine from other compounds insoluble in alcohol. Carbonic acid, passed into the solution, separates the taurine in its original state.

Hydrated oxide of lead is taken up in considerable quantity by a hot aqueous solution of taurine, the clear filtered liquid becoming only slightly turbid on cooling. On exposure to the air, it deposits a considerable quantity of carbonate of lead. An aqueous solution of taurine does not decompose carbonate of lead, even at the boiling heat.

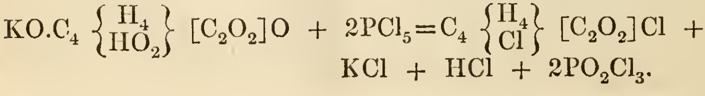
These results show that taurine is by no means an indifferent body, as it has hitherto been considered, but rather a weak acid, the acid properties of the primary compound, ethyl-sulphuric acid, being weakened in it by the substitution of amidogen for hydrogen, to nearly the same extent as, in trichloraniline, the basic properties of aniline are weakened by the introduction of chlorine.

The consideration of taurine as amido-ethyl-sulphuric acid, is further supported by its formation from isethionic acid by a process analogous to that of alanine from lactic acid.

Chloride of Chlorethyl-sulphuric Acid, and Chlorethyl-sulphuric Acid.

If isethionic acid be really constituted similarly to lactic acid, as above suggested, it may be expected to exhibit, under the influence of pentachloride of phosphorus, a transformation similar to that of lactic acid, yielding in fact the chloride of chlorethyl-sulphuric acid thus:—

Lactate of potash. Chloride of Chloro-propionic acid.



$$KO.C_4 \left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\} [C_2O_2]O + 2PCl_5 = C_4 \left\{\begin{matrix}H_4\\Cl\end{matrix}\right\} [C_2O_2]Cl + KCl + HCl + 2PO_2Cl_3.$$

Isethionate of potash. Chloride of Chlorethyl-sulphuric acid.

$$KO.C_4 \left\{\begin{matrix} H_4 \\ HO_2 \end{matrix}\right\} [S_2O_4]O + 2PCl_5 = C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right\} [S_2O_4]Cl + KCl + HCl + 2PO_2Cl_3.$$

It may further be expected that the chlorethyl-sulphuric acid, resulting from the action of water on this chloride, will be converted, by appropriate treatment with ammonia, into taurine, just as the analogously constituted compound, chloropropionic acid, is thereby converted into alanine:

$$HO.C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right\} [C_2O_2]O + 2H_3N = HO.C_4 \left\{\begin{matrix} H_4 \\ H_2N \end{matrix}\right\} [C_2O_2]O + NH_4Cl.$$

Chloropropionic acid. Alanine.

$$HO.C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right\} [S_2O_4]O + 2H_3N = HO.C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right\} [S_2O_4]O + NH_4Cl.$$

Chlorethyl-sulphuric acid. Taurine.

These expectations have been completely fulfilled by the results of the following experiments:—

To prepare chloride of chlorethyl-sulphuric acid, 60 grammes (1 at.) of finely pulverized isethionate of potash, dried at 100° C., were introduced, together with 150 grms. (2 ats.) of pulverulent pentachloride of phosphorus, into a capacious tubulated retort, the two substances being mixed together as completely as possible with a bent glass rod. The mixture, after a while, begins to get warm and to liquefy, and at length boils, with copious evolution of hydrochloric acid fumes, a large quantity of oxychloride of phosphorus distilling over at the same time into the receiver. If, after this violent action is over, the retort be gently heated, nearly pure oxychloride of phosphorus distils over at first; afterwards, when the heat is raised, a much heavier, mobile, oily liquid, having a strong pungent odour, passes over in somewhat considerable quantity. This liquid consists mainly of the chloride of chlorethyl-sulphuric acid, while in the retort there ultimately remains a dry, blackish, saline mass.

The chloride of chlorethyl-sulphuric acid, which boils at about 200° C., may be easily and completely separated from the oxychloride of phosphorus by fractional distillation; nevertheless, I have not succeeded in preparing this compound quite pure, apparently because a quantity of chloride of isethionic acid $C_4 \left\{\begin{matrix} H_4 \\ HO_2 \end{matrix}\right\} [S_2O_4]Cl$, is formed at the same time, which chloride boils at nearly the same temperature as the chloride of chlorethyl-sulphuric acid. A precisely similar observation was made by myself and Dr. Lautemann with regard to the distillation of salicylic acid, or salicylate of soda, with pentachloride of phosphorus, the chloride of salylic acid thereby produced being always more or less accompanied by chloride of salicylic acid.

The distillate which passes over in the rectification of the crude product at 200° C.—at which the boiling temperature remains to a certain degree stationary—is a nearly colourless, heavy liquid, which fumes in the air, does not mix with water, and has an intense and very persistent odour, strongly recalling that of volatile oil of mustard. Analysis gave the following numbers:

0·626 grm. burnt with oxide of copper gave 0·346 grm. carbonic acid and 0·150 grm. water, corresponding to 15·0 p. c. carbon and 2·6 p. c. hydrogen.

0·5055 grm. passed in the state of vapour over red-hot lime gave 0·7825 grm. chloride of silver = 38·3 p. c. chlorine.

0·604 grm. passed over red-hot carbonate of soda, which was finally heated in a stream of oxygen, yielded 0·905 grm. sulphate of baryta, corresponding to 20·8 p. c. sulphur.

The formula $C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}[S_2O_4]Cl$ requires

	Calculated.		Found.
C_4	24	14·7	15·0
H_4	4	2·5	2·6
S_2	32	19·6	20·5
O_4	32	19·6	,,
Cl_2	71	43·6	38·3
	163	100·0	

The somewhat too large amounts of carbon and sulphur shown by the analysis, on the one hand, and the great deficiency of chlorine on the other (a product obtained in another preparation yielded 39·2 p. c. chlorine), corroborate the supposition that the compound analysed contained a small quantity of chloride of isethionic acid.

Chloride of chlorethyl-sulphuric acid is but very slowly decomposed by water at ordinary temperatures. A drop of it covered with a large quantity of water did not disappear completely in the course of a week. Heated with water to 100° C. in a hermetically sealed tube, it dissolves somewhat readily, yielding hydrochloric and chlorethyl-sulphuric acid, and losing its odour at the same time. It dissolves easily in potash, with great evolution of heat; also in aqueous ammonia, with abundant formation of sal-ammoniac. Taurine is not produced in this last reaction, but probably the amide of amido-ethyl-sulphuric acid.

The solution of chloride of chlorethyl-sulphuric acid in absolute alcohol, even after being heated in a hermetically sealed tube to 100° C., does not yield any chlorethyl-sulphate of ethyl on addition of water.

If the strongly acid solution obtained by heating the chloride of chlorethyl-sulphuric acid with water in sealed tubes for several days be completely freed from admixed hydrochloric acid, by evaporation, first over the open fire, afterwards over the water-bath, a thickish acid liquid is obtained, consisting chiefly of chlorethyl-sulphuric acid. This acid forms crystallizable salts with oxide of lead, oxide of silver, and other bases. For the preparation of the pure acid, I have used the silver-salt, which crystallizes easily and in beautiful forms.

The solution of the crude acid diluted with a moderate quantity of water dissolves carbonate of silver with effervescence. After it has been treated, for a while with a slight excess of the carbonate of silver, without heating, but with frequent agitation, the clear filtered saline solution, which is very sensitive to the action of light, and still more to that of heat, is evaporated nearly to dryness in vacuo over sulphuric acid, being at the same time protected from the light. The crystalline mass separated from the mother-liquor, and washed with a little cold water, is well comminuted and re-dissolved in the smallest possible quantity of cold water, and on again leaving the filtered solution to evaporate in vacuo, the pure chlorethyl-sulphate of silver crystallizes out in large transparent rhombic prisms, the mother-liquor yielding an additional quantity on further concentration. Analysis gave the following numbers:

1·256 grm. of the silver-salt burnt with oxide of copper yielded 0·440 grm. carbonic acid and 0·182 grm. water = 9·5 p. c. carbon and 1·6 p. c. hydrogen.

1·015 grm. ignited with carbonate of soda in a stream of oxygen, yielded 0·987 grm. sulphate of baryta = 13·3 p. c. sulphur.

1·257 grm. precipitated with hydrochloric acid, yielded 0·703 chloride of silver = 43·1 p.c. silver.

The formula $AgO.C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right\} [S_2O_4]O$ requires

	Calculated.		Found.
C_4	24·0	9·5	9·5
H_4	4·0	1·6	1·6
Cl	35·5	14·1	—
S_2	32·0	12·7	13·3
O_6	48·0	19·1	—
Ag	108·0	43·0	43·1
	251·5	100·0	

The aqueous solution of this salt is rapidly decomposed by heat, especially at the boiling temperature, with separation of chloride of silver, isethionic acid being doubtless reproduced; but the decomposition is never complete, even after the heating has been continued for several days.

The aqueous solution of chlorethyl-sulphuric acid obtained by precipitating the silver-salt with sulphuretted hydrogen, has a strong acid reaction, and sustains a boiling heat without alteration. When concentrated by evaporation, finally in vacuo over oil of vitriol, it crystallizes in long colourless prisms, which are highly deliquescent, and melt at a moderate heat.

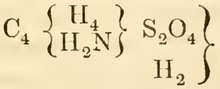
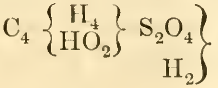
The salts of chlorethyl-sulphuric acid are easily, and to all appearance completely, decomposed by boiling with free alkali, yielding a metallic chloride and probably an isethionate. Carbonate of potash produces the same decomposition at the boiling heat.

Attempts to replace the chlorine of chlorethyl-sulphuric acid by hydrogen have, to a certain extent, given negative results. The free aqueous acid boiled with zinc, gives off a large quantity of hydrogen, without forming a trace of hydrochloric acid. Addition of sulphuric acid increases the evolution of gas, but even in this case the hydrogen does not remove any chlorine from the acid. Neither is any decomposition produced in the acid solution by the hydrogen evolved by a powerful voltaic current with two amalgamated zinc plates as the electrodes. The replacement of the chlorine by hydrogen is, however, easily effected by the electrolysis of a weak alkaline solution of an alkaline chlorethyl-sulphate, or by treating the soda-salt in the cold with sodium-amalgam.

In this respect, chlorethyl-sulphuric acid exhibits considerable resemblance to the homologous compound, chlormethyl-sulphuric acid, which I obtained in 1845 from trichlormethyl-sulphuric acid, and to which I then gave the name of chlorelayl-hyposulphuric acid.*

TAURINE.

It has already been observed that chlorethyl-sulphuric acid is converted into taurine by the action of ammonia. The transformation is easily effected as follows: Dry chlorethyl-sulphate of silver is sealed up in a strong glass tube, with a large excess of the strongest aqueous ammonia,† and the clear saline solution which is immediately formed on agitation is heated to 100° C. for several hours. The liquid remains unclouded, but, if subsequently evaporated over the water-bath, deposits a considerable quantity of chloride of silver. The dry residue dissolves in water, with the exception of the chloride of silver; the solution still retains a very small quantity of silver, which is best removed by adding a drop of hydrochloric acid immediately after the residue is dissolved.

The clear, slightly acid filtrate is evaporated to a small bulk, and mixed with strong alcohol, which precipitates a considerable quantity of taurine. The crystalline precipitate thus formed always contains, besides taurine, a variable quantity of another substance, which, when the whole is recrystallized from water, mixes with the beautiful crystals of taurine, in small white, opaque, crystalline nodules; this substance also gives off ammonia when boiled with potash-ley. I think it probable that this compound is the amide of taurine,  $\left. \begin{matrix} C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right\} S_2O_4 \\ H_2 \end{matrix} \right\} N$, mixed perhaps with the amide of isethionic acid  $\left. \begin{matrix} C_4 \left\{ \begin{matrix} H_4 \\ HO_2 \end{matrix} \right\} S_2O_4 \\ H_2 \end{matrix} \right\} N$.

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* Ann. Ch. Pharm. liv, 168, ff.

† With alcoholic ammonia, the product obtained is not taurine, but another crystalline compound, not yet investigated.

To remove this adventitious substance, the impure taurine precipitated by alcohol was boiled with potash-ley (in another preparation the same treatment was immediately applied to the crude solution of taurine filtered from the chloride of silver after addition of hydrochloric acid) till the odour of ammonia was no longer perceptible, and the highly concentrated alkaline solution was then mixed with about twenty times its volume of absolute alcohol, which, as already remarked, does not precipitate taurine from its alkaline solutions. The clear filtrate, diluted with water, evaporated, slightly acidulated with hydrochloric acid, and again evaporated to a small bulk, yields, on addition of a large quantity of strong alcohol, a copious crystalline precipitate of taurine, contaminated only with a small quantity of chloride of potassium. A better method of precipitating the taurine from its alkaline alcoholic solution might perhaps be to pass carbonic acid into it. By recrystallization from water, it is ultimately obtained in large hard crystals, and perfectly pure.

I have subsequently found that the crude chlorethyl-sulphuric acid obtained by treating the chloride of chlorethyl-sulphuric acid with water, may be used, instead of the silver-salt, for the preparation of taurine. The liquid, after being freed by evaporation from admixed hydrochloric acid, is to be neutralized with ammonia, and the ammonia-salt evaporated to dryness, and heated for some time to 100° C., in a hermetically sealed tube, with excess of saturated aqueous ammonia. The resulting solution is then to be treated in the manner above described, excepting that the larger quantity of sal-ammoniac which it contains must be removed by boiling with hydrated oxide of lead.

Taurine prepared by either of these processes agrees in every respect with that which is obtained from ox-bile, as I have convinced myself by comparative experiments. Analysis gave the following numbers:

0·3855 grm. taurine burnt with oxide of copper in a tube containing chromate of lead and metallic copper at its open end, finally in a stream of oxygen, gave 0·2715 grm. carbonic acid and 0·199 water = 19·3 p. c. carbon and 5·7 p. c. hydrogen.

0·3955 grm. ignited with carbonate of soda in a stream of oxygen, yielded 0·743 grm. sulphate of baryta = 25·8 p. c. of sulphur.

The formula $HO.C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right\} [S_2O_4]O$ requires

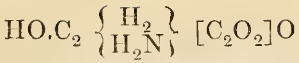
	Calculated.		Found.
C_4	24	19·2	19·3
H_7	7	5·6	5·7
N	14	11·2	—
S_2	32	25·6	25·8
O_6	48	38·4	—
	125	100·0	

Glycocine, $C_4H_5NO_4$, and taurine, $C_4H_7NS_2O_6$, which exist in bile, together with cholalic acid—doubtless in the same state of combination as glycocine and benzoic acid in the hippuric acid of urine—appear like heterogeneous compounds, when regarded merely according to their empirical formulæ; nevertheless, they are nearly related to one another, as shown by the simple mode of formation of taurine just described.

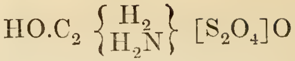
If glycocine be regarded as amido-acetic acid, that is, as carbonic acid in which one of the extra-radical oxygen-atoms is replaced by amido-methyl, then taurine must be regarded as an analogous derivative of sulphuric acid, excepting that one of the extra-radical oxygen-atoms is replaced by amido-ethyl instead of by amido-methyl, as shown by the following formulæ:

$$\underset{\text{Glycocine.}}{HO.C_2 \left\{ \begin{matrix} H_2 \\ H_2N \end{matrix} \right\} [C_2O_2]O} \qquad \underset{\text{Taurine.}}{HO.C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right\} [S_2O_4]O.}$$

Since it is known that, besides glycocine, many similarly constituted homologous derivatives of the fatty acids—especially leucine (amido-propionic acid)—are widely diffused in the animal body, the observation that the functions of taurine in the bile-compounds, is precisely similar to that of glycocine, lends some degree of probability to the supposition that the animal body contains, besides taurine, other similarly constituted homologous derivatives of sulphuric acid, especially amido-methyl-sulphuric acid, the direct analogue of glycocine, and amido-amyl-sulphuric acid, analogous to leucine, both of which compounds perhaps enter into the composition of many animal substances rich in sulphur, such as horn, hair, &c.


$HO.C_2 \left\{\begin{matrix} H_2 \\ H_2N \end{matrix}\right\} [C_2O_2]O$

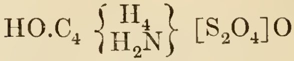
Amido-methyl-carbonic acid.
(Glycocine).


$HO.C_2 \left\{\begin{matrix} H_2 \\ H_2N \end{matrix}\right\} [S_2O_4]O$

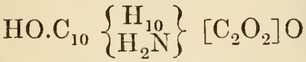
Amido-methyl-sulphuric acid.

$HO.C_4 \left\{\begin{matrix} H_4 \\ H_2N \end{matrix}\right\} [C_2O_2]O$

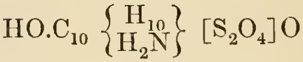
Amido-ethyl-carbonic acid.
(Alanine).


$HO.C_4 \left\{\begin{matrix} H_4 \\ H_2N \end{matrix}\right\} [S_2O_4]O$

Amido-ethyl-sulphuric acid.
(Taurine).


$HO.C_{10} \left\{\begin{matrix} H_{10} \\ H_2N \end{matrix}\right\} [C_2O_2]O$

Amido-amyl-carbonic acid.
(Leucine).


$HO.C_{10} \left\{\begin{matrix} H_{10} \\ H_2N \end{matrix}\right\} [S_2O_4]O$

Amido-amyl-sulphuric acid.

I regard it as by no means a thankless problem to search for these and other compounds homologous and analogous to taurine in the animal body, and especially in the secretions which are peculiarly rich in sulphur. From the above-described mode of formation of taurine, we might also expect that the artificial preparation of these other compounds would not be difficult. I am at present engaged with the attempt to convert chlormethyl-sulphuric acid—a compound very closely resembling chlorethyl-sulphuric acid—by the action of ammonia, into amido-methyl-sulphuric acid, an acid which may be expected to exhibit considerable resemblance to taurine.

XX.—*On the Determination of Alkalies in Fire-clays and Fire-bricks.*

By G. Gore.

As the process of bringing pulverized fire-clay, or fire-brick, into solution by digestion with aqueous (or treatment with gaseous) hydrofluoric acid, for the determination of the alkalies contained in it, is very tedious,—and as the other process employed for the same purpose, viz., mixing the substance with nitrate of baryta, and subjecting it to an intense white heat, does not produce a perfectly fused and fluid mixture, but only agglutinates the materials into a semi-fused mass,—I have adopted the following method, which has proved in my experience more effectual and satisfactory.

Three parts of perfectly dry nitrate of baryta, very finely pulverized, to prevent decrepitation, were mixed with three parts of equally dry and finely powdered fluoride of barium, and one part of the finely pulverized clay or brick. The mixture was projected, in successive portions, into a red-hot platinum crucible, a little of the nitrate and fluoride, unmixed with the clay, being reserved and spread upon the top, and the mixture then heated as highly as possible over a Bunsen's burner. The crucible was then transferred to a Griffin's analytical gas furnace, and heated during fifteen minutes to a still higher degree, then removed and cooled.

Any particles of the mixture which now adhered to the edge of the crucible were scrupulously removed and added to the general contents. The crucible was placed in a Griffin's gas blast furnace, and covered with a stout sheet of platinum, and heated to the maximum power of that furnace during twenty minutes; the lid was then removed; the contents of the crucible (which were perfectly liquid) were poured into a shallow, massive vessel of cast-iron, and a cold block of cast-iron at once placed upon the heated mass. It quickly decrepitated into numerous small pieces, which were collected, and carefully crushed still smaller in a steel crushing mortar; and the resulting coarse powder, together with the crucible, and any portions adhering to it, was placed in a platinum dish, and covered with pure sulphuric acid. A very moderate heat was now applied, the decomposition proceeded rapidly, and the resulting sulphate of baryta floated upon the acid as a bulky scum; as soon as the action declined, further heat was applied, and the contents of the vessel were evaporated to perfect dryness, to remove excess of sulphuric acid; the residue was now digested with abundance of hot water, and the liquid part, containing the whole of the alkalies in solution, was then treated in the usual manner. The portion of the process here described occupied about four hours.

The results obtained in three different analyses agreed very closely with each other and with three analyses of the same substance made with aqueous hydrofluoric acid.

XXI.—*Note on Professor Bolley's Communication "On some Physical Properties of the Alloys of Tin and Lead."*

By A. Matthiessen, F.R.S.

In the last number of the "Journal of the Chemical Society" (vol. xv., p. 30), Professor Bolley gives an account of Mr. Pillichody's research into some physical properties of the alloys of tin and lead.

A table is there given purporting to be a comparison of the values found by Kupffer, Long, Thomson, and Pillichody, for the specific gravities of these alloys. Long's determinations, here quoted, having been made at my request and recorded in my paper, "On the Specific Gravity of Alloys,"* I feel bound to point out a mistake into which Professor Bolley has fallen with regard to what he calls the *calculated specific gravities* in the table referred to. These are, he says, "calculated from the quantities and specific gravities of the component metals;" whereas it is sufficiently obvious, and I have already drawn attention to the point in my paper, quoted above, that they ought to be calculated, not from the *quantities* (or weights) but from the *volumes* of the component metals; for, when no expansion or contraction takes place, the specific gravities of the components take part in the specific gravity of the compound in the ratio of their relative volumes, and not in the ratio of their weights.

Hence the great apparent differences between the specific gravities of the alloys of tin and lead as found by Long, and the calculated values given in Bolley's table, the latter being, as I have said, calculated according to a wrong method. By reference to my paper in the "Philosophical Transactions," it will be seen that the experimental specific gravities found by Long agree even more closely with the numbers calculated according to the right method than do those of Kupffer, whereas the contrary appears from this table. The reason of this is, that the calculated specific gravities, with which Kupffer's results are here compared, are those given by himself, and are rightly calculated.

To show clearly the incorrectness of the method of calculating the specific gravities by which those in the table were calculated, let us see what the theoretical specific gravity will be of an alloy composed of 1 grm. aluminum and 1 grm. platinum, of course under the supposition that no contraction or expansion takes place. Then, according to the method employed in Professor Bolley's table, the specific gravity will be equal to $\frac{1 \times 2{\cdot}5 + 1 \times 21{\cdot}45}{1 + 1} = 11{\cdot}97$, taking the specific gravity of aluminum equal to 2·5, and that of platinum equal to 21·45, whereas the theoretical specific gravity of the alloy is only 4·46: for if we assume that no contraction or expansion takes place when the two metals alloy with each other, then we may look on such an alloy, when taking its specific gravity, as if the two metals were hanging side by side in the water. Now, 1 grm. of aluminum will displace 0·4 grm. water, and 1 grm. platinum 0·047 grm. If, therefore, the theoretical specific gravity of the alloy be required, it will be the weight of the two metals divided by the quantity of water displaced by them, or $\frac{2}{0{\cdot}4 + 0{\cdot}047} = 4{\cdot}46$.

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* Phil. Trans. 1860, p. 177.

It further appears, that, when the correction I have indicated is introduced, Mr. Pillichody's experiments confirm those of Long, as to the greatest expansion taking place in the formation of the alloy $SnPb_2$, and not of the alloy SnPb, as stated, by Professor Bolley.

XXII.—*Observations on Silica.*

By ARTHUR H. CHURCH, B.A.

THE recent researches of Mr. Graham in dialysis have shown us how to prepare a pure aqueous solution of silica of considerable strength and with great ease. Pure water, according to Kirwan, is capable of taking up no more than one-thousandth part of its weight of hydrate of silica freshly precipitated, while there is no difficulty in obtaining, by the dialytic method, a liquid containing fourteen per cent. of that substance. The other processes for procuring silica in solution are less satisfactory, for it is difficult to free the product from hydrosulphuric acid when sulphide of silicon is used; and on heating gelatinous silica with water in a glass tube under pressure, the glass is acted on, and a portion of alkaline silicate formed.

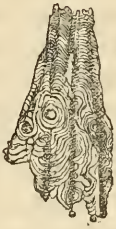
A solution of silica containing more than 0·5 per cent. of the anhydride cannot be kept long without change; but I have observed no alteration as to transparency or fluidity in a solution containing 0·47 per cent. after the lapse of three months. With respect to stronger solutions, the process of gelatinization is generally more or less gradual. Freshly prepared, a solution containing 3 per cent. of anhydrous silica was perfectly limpid, and nearly as mobile as water; after the lapse of six days, it acquired the consistence of glycerin, and then rapidly became ropy, the silica separating in gelatinous masses. The solution in this case was kept in a well-stoppered bottle. Solutions of silica obtained by dialysing an alkaline silicate after addition of hydrochloric acid, seem, according to my experiments, to retain their fluidity longer than those of the same strength where sulphuric acid has been used; and as a general rule, the purer the solution and the freer from acids and salts, the longer may it be preserved without change.

The chlorides of barium, strontium, and calcium, and many other salts, produce no immediate precipitate in an aqueous solution of silica; but solutions of the alkaline earths at once throw down the whole of the dissolved substance; or, if they be added in insufficient quantity, the silicate formed causes the remainder of the silica to separate as a jelly. This action is still more prompt if the carbonates of calcium, strontium, or barium be made to react upon the silica solution. One milligramme of pure carbonate of calcium in fine powder was put at the bottom of a beaker, and then 100 cubic centimetres of a 1 per cent. silica solution were poured upon it: in ten minutes, the mixture was a firm jelly, and the vessel could be inverted without the loss of any of its contents.

I cannot but think that this singular deportment of the aqueous solution of silica with the carbonates of the alkaline earths tends to throw great light upon several important geological and mineralogical questions. Silica, we know, is almost an invariable constituent of the waters of the earth, and in several cases it exists in solution in considerable quantity, rather as silicic acid than as an alkaline silicate. Several springs in Iceland, at Luzon in the Philippine Islands, and in New Zealand, deposit a beautiful quartz-sinter, containing scarcely more sodium and potassium than common flint. But the action of far weaker solutions of silica may, I believe, be traced very frequently in less striking but more common conditions. I have endeavoured to test this supposition by a series of experiments, an example of which I will now describe.

A curious silicified substance, at once a mineral and a fossil, occurs in the triassic red conglomerate of Torbay and its neighbourhood; similar, if not identical, bodies are found in other parts of Great Britain, and also in a few foreign localities. This mineralized fossil, to which the name of "Beekite" has been assigned, presents itself under such a variety of aspects as to baffle description, so far as regards its physical features; its chemical composition is more constant. Originally corals or shells, and therefore consisting in great measure of carbonate of calcium, beekites have become so modified in constitution as to contain on an average no less than 92 per cent. of silica; a small but variable amount of calcium occurs in them, but this exists as silicate rather than carbonate; a few exceptional cases have been noted, where the process of silicification has been arrested before completion, and where the interior of the beekite may be completely dissolved away by hydrochloric acid, though the outside is not affected by this reagent. I have attempted to transform corals and shells into a substance resembling that of which beekites consist. The trial was made in this wise. A fragment of recent coral was fitted tightly into the neck of a funnel, and a solution of silica in water containing dissolved air and carbonic acid was allowed to fall upon it drop by drop. The liquid which filtered through contained much carbonate of calcium, but no silica, while the coral ultimately retained very little carbonate of calcium. The silica-solution should be very dilute, about 0·15 per cent., otherwise part of the silica will gelatinize on the surface of the coral and prevent further action.

I have endeavoured also to illustrate, by means of the aqueous solution of silica, that tendency to deposition, in a circular or globular form, which is so marked a characteristic of many siliceous minerals, such as quartz-sinter, eyed agate, bubble-chalcedony, and especially beekite. In the latter case, the surface of the specimen generally shows a number of tubercles surrounded by systems of concentric ridges. So strongly is this circular tendency developed in some instances, that a fragment of a silicified pecten, in my possession, shows a system of rings, partly situated in a furrow of the outer aspect of the shell, then bent upwards to follow the natural curve of a ridge, and then turned down into another furrow. (The inner and more level aspect of this fragment is shown in Fig. 1.) I was anxious to see whether such circular forms could be attained artificially, and the more so as Mr. Rainey has obtained similar globular crystals of carbonate of calcium. Although I have not at present arrived at any definite conclusion on the subject, I have yet observed, in working with an aqueous solution of silica, several phenomena which may suggest an answer to the question. Among these phenomena the following may be mentioned: the irregular spherical masses into which a solution of silica often dries up in the air, the faint curved markings developed in a piece of oyster-shell after artificial silicification (see Fig. 2), and the singular narrow flakes into which the film of silica, forming round and just above the margin of its aqueous solution, when evaporating in a dish or beaker, divides. These narrow strips curl inwards, the ends meet, and the rings or sections of cylinders thus formed accumulate in the liquid, presenting an appearance of great interest, the origin of which was not at first sight apparent (see Fig. 3).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XXIII.—*On Isoprene and Caoutchin.*

By C. Greville Williams.

[Abstracted from the "Philosophical Transactions," 1860, p. 241.]

The products of the destructive distillation of caoutchouc have been studied by several chemists. The results hitherto obtained are, however, quite irreconcilable. Gregory* appears to have been the first to direct attention to them, but it is evident that even at the time of writing his "Handbook of Organic Chemistry" he was far from considering the true nature of the products as having been ascertained; for, at p. 316, he says: "When exposed to heat, caoutchouc first melts and then distils, yielding a mixture of several oily liquids, all of which, as well as pure caoutchouc itself, are carbo-hydrogens. Some of these oils boil at 90°, others at 680° Fahr.; and at intermediate points I found that one highly rectified oil which boiled at 96°, and had the composition of olefiant gas, yielded when acted on by sulphuric acid, an oil which boiled at 428°, and had the same composition. But most of these oils have the composition of oil of turpentine, C_5H_4, or $C_{10}H_8$. One of them, called *caoutchin*, gives with chlorine an oil, $C_{10}H_8+Cl$." Now the above statement contains undoubtedly the best account that could be given in so short a space of the results that had been obtained up to the time of publication of the work alluded to; but the account is somewhat confused, because the various observers all differ immensely in their results. The expressions C_5H_4 and $C_{10}H_8$, as used by Gregory, merely indicate arithmetical relations, and are not to be received as definite formulæ; for, in the first place, C_5H_4 is, according to our present views, an impossible formula†, and in the next, caoutchin is $C_{20}H_{16}$, not $C_{10}H_8$. No chemist up to the present time has proved a hydrocarbon of the formula $C_{10}H_8$ (= 4 volumes of vapour) to exist among the products of the distillation of caoutchouc. Such a formula, if proved, would be interesting, because, turpentine being the starting-point for Kopp's empirical formula for boiling-points, any substance having exactly half the number of atoms of carbon and hydrogen, with the same vapour-volume, would serve as the point of departure of numerous speculations upon boiling-points generally. The results of M. Bouchardat‡ are curious, and not easy to understand. He obtains olefiants and eupione, but no bodies of the formula $n\ (C_5H_4)$, while Himly§ obtains bodies of the latter formula and no olefiants. The annexed table contains the results of the three chemists alluded to.

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* Ann. Ch. Pharm. xvi., 61.

† $C=6,\ H=1,\ O=8$.

‡ Ann. Ch. Pharm. xxvii., 30.

§ Ibid. p. 40.

Name of observer.	Fluid found.	Boiling-point.	Density.	
			Liquid.	Vapour.
Gregory	C_nH_n	36° C.	0·654	
Bouchardat	C_5H_8	below 0	0·630 at 4°	
Bouchardat	Caoutchène (C_nH_n)	14·5	0·650	
Bouchardat	Eupione (?)	51	0·690 at 15°	
Himly	C_5H_4 (?)	30 – 40		
Himly	Caoutchin ($C_{20}H_{16}$)	171	0·842	4·461
Bouchardat	Hévéène (C_nH_n)	above 315	0·921 at 21°	

Results so contradictory would almost lead one to suppose that caoutchouc, like castor-oil, yielded different products according to the temperature; but in that case, the distillate obtained in a carefully conducted experiment should contain bodies belonging to the olefiants and the terebenes; this, however, is not the case. The weight of evidence appearing to prove olefiants to be the principal products, I had some hopes that caoutchouc, if carefully distilled, would yield hydrocarbons from which I might obtain certain at present unknown hydriodic ethers and their derivatives, in accordance with reactions first imagined by M. Berthelot, thus:—

$$\underbrace{C_nH_n + HI}_{\substack{\text{Olefiant plus}\\ \text{hydriodic acid.}}} = \underbrace{(C_nH_{n+1}) + I}_{\substack{\text{Iodide of alcohol-}\\ \text{radical.}}}$$

but I soon found that caoutchouc, when carefully distilled in iron vessels, yielded no olefiant whatever. This is, moreover, in perfect accordance with experiments made by me some years ago,* in which I showed that caoutchouc, like many other oils, decolorized the same quantity of bromine as oil of turpentine. A repetition of this experiment, made with great precaution to ensure success, will be found further on.

The distillation was conducted with care in an iron alembic, the lowest temperature being used consistent with the distillation of oils. In fact I even stopped the distillation before the whole of the last oil, hévéène, came over, in order to ensure the decomposition taking place in the simplest manner. The crude distillate was very fœtid, and contained traces of volatile bases derived from the decomposition of a minute trace of vegetable caseine in the caoutchouc. The bases were removed by agitation of the oil with dilute sulphuric acid; the latter was then got rid of by washing with water, which, in its turn, was subsequently removed by digestion with sticks of potash. The fluid thus prepared was easily separated by fractional distillation into two portions, one boiling between 37° and 44° C., and the other between 170° and 180°. The fractional separation of the hydrocarbons in the crude distillate affords a very instructive example of the extraordinary extent to which boiling-points are lowered by successive rectifications. In the first rectification the product was very small, below 116° C. The greater part distilled between 116° and 193°. Only one-half came over below 204°. In the second rectification, a large fraction was obtained between 40° and 50°, then scarcely any distilled until between 170° and 180°, which latter fraction was very large. At 171°, the thermometer was often perfectly steady while an ounce distilled over, the entire contents of the retort not being much more than one and a half ounce. The lower fraction oscillated between 36° and 44°, the variability in its boiling-point being principally due to the presence of oxygen; for, by careful and repeated rectifications over sodium, it may be made to distil almost entirely between 37° and 38°. This fluid lies at the boundary line between gases and liquids; it is scarcely possible to wet the hand with it; and if poured from a moderate height in small drops, it is volatilized before reaching the floor. A very good way of observing the influence of small pressures upon its physical condition, consists in passing a few drops into a mercurial eudiometer standing vertically. The warmth of the hand applied to the top of the instrument is sufficient to convert it into vapour; but if the position of the eudiometer be then altered so as to stand almost horizontally, the increase of pressure is sufficient to condense the gas into a liquid, and, on the other hand, it is instantly vaporized again on restoring the eudiometer to its original position.

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* "On a Process for estimating the Equivalents of some Fluid Hydrocarbons by means of Bromine," Chemical Gazette, 1853.

This hydrocarbon possesses a property which, even more than its extreme volatility, renders it troublesome to the analyst. Unlike very volatile fluids in general, it lines with a slight film of carbon the bulbs in which it is contained during combustion. It is true that the amount thus left is very small, but it is sufficient to render an exact determination of the carbon difficult. It being of course necessary to have all the apparatus, oxide of copper, &c., as cold as possible, it was also not easy to keep the hydrogen as low as could be desired. The substance used in the first three analyses boiled between 37° and 38°, and was prepared from caoutchouc. The fourth and fifth analyses were made on a product from gutta percha. No. IV. boiled between 42° and 43°, and No. V. between 43° and 44°.

	Experiment.					Mean.	Calculation.		
	I.	II.	III.	IV.	V.				
Carbon .	88·3	87·8	87·9	87·8	88·1	88·0	C_{10}	60	88·2
Hydrogen	12·0	12·0	12·1	12·2	12·3	12·1	H_8	8	11·8
								68	100·0

leading to the empirical relation

$$n\,(C_5H_4).$$

Although the boiling-point indicated the value of n to be not greater than 2, it is plain that the liquid might possibly have a higher formula. The atomic weight was therefore determined from the density of the vapour, assuming it to possess the usual condensation to four volumes.

Mean of experiments.	Theory, $C_{10}H_8 = 4$ volumes.
2·44	2·3493

I have given the substance thus examined the name of *isoprene.*

The specific gravity of the liquid at 20° C. was found to be 0·6823.

It will be seen that none of the hydrocarbons examined by Gregory, Himly, or M. Bouchardat can be identified with that just described; and although the formulæ C_5H_4 and $C_{10}H_8$ have often been vaguely applied to the numerous isomers of turpentine, yet none of the hydrocarbons obtained by the above chemists have been shown to contain $C_{10}H_8$ *for four volumes of vapour*. The hydrocarbon discovered by Couerbe* in the fluid obtained by the powerful compression of resin gas, although of the same composition, differs too much in density (0·709) and boiling-point (50°) to be considered as identical.

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* Ann. Ch. Phys. lxix., 184. J. pr. Ch. xviii., 165. Gmelin's Handbook, x., 411, Cavendish Society's Translation.

Action of Atmospheric Oxygen on Isoprene.

If isoprene be left in a partly filled bottle for some months, it gradually loses its fluidity, and at last even becomes quite viscid; at the same time it is found to have acquired powerful bleaching properties. It readily decolorizes sulphate of indigo, and, under certain circumstances, converts sulphide of lead into sulphate. It is, in fact, ozonized.

Schönbein was the first to show that oil of turpentine absorbed ozone when kept for a long time; and I subsequently observed several cases where ozone was capable of existing in contact with organic and inorganic matters without exerting any material action on them so long as the temperature was kept down. In these instances, immediately the heat rose beyond a certain point, the substance in contact with the ozone underwent oxidation. Thus, if a slip of lead test-paper be exposed to the vapours of sulphide of hydrogen until the paper has acquired a deep brown colour, and a drop of an ozonized oil be placed on it, no change ensues at ordinary temperatures; but if the paper moistened with the oil be warmed until the latter begins to volatilize, the sulphide is immediately oxidized and bleached.

But the most remarkable phenomenon perhaps yet known in connection with the ozonization of essential oils, takes place on submitting ozonized isoprene to distillation. If the temperature be kept as low as is compatible with the volatilization of the unaltered portion of the oil, a colourless limpid fluid distils over, having the composition and boiling-point of pure isoprene. As the operation proceeds, the fluid thickens, causing the temperature to rise somewhat suddenly. The ozone at this point instantly begins to act with energy, a cloudy vapour rises, accompanied by an intensely sharp odour, and the contents of the retort instantly solidify to a pure white, spongy, elastic mass, having, when successfully prepared, but slight tendency to adhere to the fingers. When pure, it is opaque; but if allowed to become exposed to the air, especially when warm, it becomes transparent, first on the edges, and subsequently throughout the whole mass. When burnt, it exhales the peculiar odour hitherto considered characteristic of caoutchouc itself. It is not easy to prepare or to preserve this substance of definite composition. If the heat be allowed to rise too rapidly during its formation, it becomes decomposed; and if not heated sufficiently, a portion of the original hydrocarbon obstinately adheres, in spite of its extreme volatility when separate. However prepared, its composition is that of isoprene plus oxygen. If sufficient care be taken, the oxidation is perfectly definite. A specimen prepared with every precaution, and immediately analysed, afforded, on combustion with oxide of copper and oxygen gas, numbers agreeing with the formula $C_{10}H_8O$.

As regards the true formula of this substance, there is reason to suppose that the expression $C_{10}H_8O$ does not correspond to four volumes of vapour; but as it is not volatile without decomposition, and as its properties forbid any hope of its yielding compounds from which the true equivalent might be deduced, I am at present compelled to rest satisfied with obtaining the simplest arithmetical relation between the elements.

The above-described substance is, it is believed, unique in its characters, whether we regard its composition as the directly formed oxide of a hydrocarbon, or the mode of its production by the influence of ozone.

Caoutchin.

The formula $C_{20}H_{16}$ derived by M. Himly from his experiments upon the oil boiling between 171° and 173° is perfectly correct. My analyses confirm his results as regards both the per-centage composition and the vapour-density; the latter is, by my experiments, 4·647; by Himly's, 4·461; by calculation (4 vol.), it is 4·6986.

On the Relation between the first and second Hydrocarbons produced by distillation of Caoutchouc.

We are now, for the first time, in a position to understand the true connection between the two hydrocarbons which have been described. The relation between them is the same as that between amylene and paramylene, and, as in the case of those bodies, the second is twice as heavy in the state of vapour as the first.

The boiling-point of the bodies show very strongly the limited power of empirical formulæ, even when (like those of Kopp and Gerhardt) founded on the accurate observation of a vast number of bodies. Thus, amylene $C_{20}H_{20}$, containing four atoms of hydrogen more than caoutchin, should boil, according to Gerhardt's law, $15 \times 2 = 30°$ lower than that body, whereas the boiling point is only 11° lower. Again, amylene, containing two atoms of hydrogen more than isoprene, should boil 15° lower, whereas it boils 2° higher.

The reduplication of a formula has not the same *relative* influence upon the boiling-point of amylene that it has upon that of isoprene; thus—

Paramylene,	$C_{20}H_{20}$, boils at	160°	Caoutchin,	$C_{20}H_{16}$, boils at	171°
Amylene,	$C_{10}H_{10}$, boils at	39°	Isoprene,	$C_{10}H_{8}$, boils at	37°
Difference . . .		121	Difference . .		134

Oil of turpentine boils at 160°, and is taken as the pivot round which the boiling-points of hydrocarbons should arrange themselves at distances proportioned to the number of atoms of carbon and hydrogen in their formulæ; yet caoutchin, which not only has the same formula, but gives almost identical reactions, boils at 171°, eleven degrees higher, and very near that of carvene, which is 173°.

Comparative experiments on the Action of Bromine on Caoutchin and Oil of Turpentine.

M. Himly had observed that chlorine and bromine act upon caoutchin, and that the products when distilled over a base, afforded an oil containing less hydrogen than caoutchin. He did not examine the nature of the reaction more closely.

I mentioned, at the commencement of this paper, that I had several years ago made an experiment on the mutual action of bromine and caoutchin, which led me to believe the latter to belong, not to the olefiants, but to the vast group of hydrocarbons isomeric with oil of turpentine. But that experiment having been made with the bromine and hydrocarbon undiluted, and, moreover, the caoutchin not having been prepared by myself, I considered it necessary to repeat it with several precautions not then observed.

The action of bromine upon the terebenes is peculiar, one atom, or four-volume equivalent, always requiring exactly four atoms of bromine to produce a colourless fluid. If the hydrocarbon and the bromine be diluted, the former with alcohol, the latter with water, the experiment may be made with considerable precision. For the purpose of comparing the isomers, I prepared some freshly dried and rectified turpentine and caoutchin. They were diluted with sufficient alcohol for each of the resulting liquids to contain exactly ten per cent. of hydrocarbon. The bromine employed was in the state of a weak solution in water, twenty cubic centimetres containing 0·2527 of bromine. A small flask containing twenty cubic centimetres with the stopper in its place, was employed each time to measure the bromine-water, which was transferred to a large stoppered flask, every precaution being taken to prevent loss. The diluted hydrocarbon was then gradually dropped into the bromine-water from a Schüster's alkalimeter containing a weighed quantity. Considerable agitation was applied after each addition. When the bromine-water was nearly decolorized, the liquid was added very cautiously, and an interval of about half a minute allowed to elapse between each addition. When the fluid had become perfectly colourless, the alkalimeter was reweighed. The following numbers were obtained in eight experiments made in the manner described :—

Mean of turpentine experiments.	Mean of caoutchin experiments.
0·1074	0·1091

The identity of behaviour of caoutchin and oil of turpentine becomes very evident from the above experiments. The mean of the caoutchin results is nevertheless somewhat higher than that of the turpentine series; I ascribe this to caoutchin being, to a very slight degree, more sluggish in its action than oil of turpentine.

Action of Bromine on Isoprene.

I was exceedingly desirous of making experiments with weighed quantities of isoprene and bromine, in order to compare it with caoutchin. With this intent I made a solution of it in alcohol, the strength being the same as the turpentine and caoutchin solutions. But it was impossible to obtain the wished-for results, owing to the manner in which the isoprene volatilized from the solution while pouring it into the bromine-water.

Isoprene combines explosively with bromine, even in presence of seventy or eighty times its volume of water. When the vessel containing the bromine at the bottom and the isoprene on the surface is shaken, union takes place with a loud noise and considerable evolution of heat. A fine mobile bromine-compound is the result. When cohobated with excess of hydrate of potash, the greater portion is entirely decomposed, yielding a black mass, the distillate having the same odour as that evolved under similar circumstances by the higher olefiants, but accompanied by a substance so irritating to the eyes as to render it very distressing to manipulate. On placing about one ounce in a flask, and adding a fragment of hydrate of potash to neutralize it, an explosion took place, the fluid being thrown in my face, and causing the most intense pain in the eyes. For several days no person could enter the laboratory without incurring great pain, accompanied by profuse lachrymation. The substance having in this unfortunate manner been lost, I am compelled to defer a more minute investigation of it.

Conversion of Caoutchin into Cymole and Paracymole.

In Gerhardt's classification of organic bodies, oil of turpentine is made to belong to the cymenic series; and it is even stated that Deville, by passing turpentine and carbonic acid through a tube heated to dull redness, obtained an oil which appeared to contain $C_{20}H_{14}$; carbonic oxide, water, and empyreumatic products being formed simultaneously. Disregarding the empyreumatic bodies, the following equation may be considered to explain the nature of the reaction:—

$$\underbrace{C_{20}H_{16}}_{\substack{\text{4 vols. oil of}\\ \text{turpentine.}}} + \underbrace{C_2O_4}_{\substack{\text{4 vols. carbonic}\\ \text{acid.}}} = \underbrace{C_{20}H_{14}}_{\substack{\text{4 vols.}\\ \text{cymole.}}} + \underbrace{2HO}_{\substack{\text{4 vols.}\\ \text{water.}}} + \underbrace{2CO}_{\substack{\text{4 vols. carbonic}\\ \text{oxide.}}}$$

Some experiments made by me a considerable time ago with oil of turpentine, led me to conceive the idea of converting it into cymole, or an isomer, by the alternate action of bromine and a highly electro-positive metal, and the identity in certain cases of the reactions of oil of turpentine and caoutchin rendered it probable that a similar product would be yielded with the latter. Experiment has completely confirmed this supposition.

If to a quantity of bromine and water in a stoppered flask caoutchin be gradually added, and the flask be shaken after each addition, a sharp hissing sound is heard, and combination takes place with great energy and considerable rise of temperature; at the same time a heavy oil, red at first but finally colourless, sinks to the bottom. The product when cold is as viscid as treacle. Its characters do not offer any great guarantee for purity; and the production of hydrobromic acid at the same time indicates that while one portion of the halogen combines with the caoutchin, another seizes the most easily removable of its atoms of hydrogen, and yields the acid which is found dissolved in the water.

I examined the reaction which takes place with turpentine under these circumstances some years ago, but at that time I was not fully alive to the true explanation, because I had not treated the resulting oil with alcoholic potash or sodium. The analyses I then made indicated the formula of the oil from turpentine to be $C_{20}H_{15}Br.\ 2Br.\ 2HO$. One equivalent of hydrobromic acid was always found in the watery fluid. Assuming this to be correct, as I have no doubt it is, we have

$$C_{20}H_{16}+4Br+2HO=C_{20}H_{15}Br.\ 2Br.\ 2HO+HBr.$$

Every four equivalents of bromine yield, therefore, one equivalent of hydrobromic acid; and in an experiment where 33·2 parts of bromine were employed, 8·2 of hydrobromic acid were found in the aqueous fluid. If the above equation be correct, 8·4 should have been obtained.

The oil produced as above from caoutchin yields, when heated, torrents of hydrobromic acid, and an oil distils over containing less bromine and hydrogen. On cohobating it with sodium in excess, a very fragrant and perfectly colourless hydrocarbon was produced, distilling between 171° and 200°. It was received in four portions: *a*, between 171° and 177°; *b*, 177° to 181°; *c*, 181° to 186°; and *d*, 186° to 200°. A yellowish oil remained behind at this point; it required a very much higher temperature for distillation, and on cooling deposited a few very minute crystals.

Caoutchin and turpentine behave in a precisely similar manner with the above reagents; and it is worthy of observation that the resulting hydrocarbon has the same peculiar odour, from whichever source it is prepared.*

Analysis yielded numbers agreeing completely with the formula $C_{20}H_{14}$, which is that of cymole. Moreover, the density of the liquid, 0·8664 at 20°, was almost the same as that given by Gerhardt, namely, 0·8610 at 14°.

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* Since writing the above, I have compared the cymole from caoutchin, and that from oil of turpentine, with a specimen of the same hydrocarbon, prepared with great care from oil of cumin by my friend Mr. Church; the odour in each case was absolutely identical.

I could have wished to give equations expressive of the entire decompositions which take place, and it would be easy to do so were I to disregard, or consider as merely accidental, the substances formed at the same time. When the brominized oil is distilled, before or after treatment with alcoholic potash, nearly fifty per cent. of loss is incurred. The retort contains a black carbonaceous mass, occupying two-thirds of its capacity. A similar phenomenon occurs in the treatment with sodium; and at the same time, as already observed, a certain portion of caoutchin or turpentine, as the case may be, is regenerated.

The yellow oil of high boiling-point previously alluded to exists in very small quantity among the products formed by the action of sodium on brominized caoutchin; probably not more than one-tenth of the distillate boils above 200° C., whereas the yellow oil boils only a little below 300° C. The quantity in my possession was far too small to allow of a determination of this point. In composition, however, it agreed with that of cymole.

The crystalline substance was in exceedingly minute quantity. It is far from impossible that it may be the radical thymyl formed from its hydruret cymole by the action of the bromine. As it would have the composition $C_{40}H_{26}=2C_{20}H_{13}$, the probability is that it would be a crystalline solid.

The exceedingly high boiling-point of the yellow oil is such strong evidence of its being a polymeric condition of cymole, that I have provisionally named it *paracymole*.

Conversion of the Cymole from Turpentine and Caoutchin into Insolinic Acid.

Although the experiments detailed left little doubt of the identity of the cymole from turpentine and caoutchin with that from cumin oil, still the number of isomeric bodies continually being discovered is so great, that it was highly desirable to make a crucial experiment. The exceedingly characteristic properties of isolinic acid rendered it peculiarly suitable in the present instance. Dr. Hofmann has shown it to be a product of the oxidation of cuminic acid and cymole under the influence of chromic acid. The quantity of cymole in my possession was so small (about two drachms), that there would have been little hope of success had the reaction been less definite. On cohobating it with 8 parts of sulphuric acid, 8 pts. of bichromate of potash, and 12 pts. of water, for a few minutes, white flocks became apparent; they continually increased until their bulk equalled that of the cymole employed. The crude acid was dissolved in ammonia, and, after filtration, precipitated by hydrochloric acid. It was washed, first with warm water, then with boiling alcohol, and finally with ether. Thus purified it was quite colourless. It was then dissolved in ammonia, and the solution evaporated until crystals of the acid salt began to form. The solution, rendered faintly alkaline by the cautious addition of ammonia, was precipitated by nitrate of silver, care being taken to keep it slightly alkaline, to prevent the separation of any insolinic acid. The salt, after drying at 100° until it ceased to lose weight, was ignited, during which operation it evolved the peculiar aromatic odour so characteristic of all the insolinates when heated strongly. In this manner I prepared three specimens, one from turpentine, another from caoutchouc, and a third from gutta percha. All three gave, by analysis, results corresponding sufficiently with the formula

$$C_{18}(H_6Ag_2)O_8.$$

Action of Sulphuric Acid on Caoutchin.

On slowly adding caoutchin to sulphuric acid (sp. gr. 1·845) in great excess, the latter becomes warm, and the greater part of the hydrocarbon dissolves, traces of sulphurous acid being at the same time evolved. On the addition of water, the greater part of the caoutchin rises in an altered state to the surface; it is in the form of a thick adhesive fluid of the consistence of molasses. On saturating the acid solution with chalk, a very small quantity of the lime-salt of a conjugate sulphuric acid was obtained. It is excessively soluble in water, and deposits small granular crystals from a concentrated solution. Dried at 200° C. it gave, by analysis, results agreeing with the formula $C_{20}H_{15}CaS_2O_6$.

On the Composition of Caoutchouc.

The only analyses of caoutchouc which I have seen are those of Faraday and the late Dr. Ure. That of the latter chemist is obviously incorrect, as he obtained 90 per cent. of carbon and only 9.1 of hydrogen, a result incompatible with the phenomena which take place under the influence of heat.

Faraday's analysis, made in the year 1826, probably exhibits almost exactly the true composition of pure caoutchouc. It gave carbon 87·2 and hydrogen 12·8 per cent. These numbers would require to be slightly modified, in consequence of the atomic weight of carbon, as now received, having a somewhat different value to that which was admitted at the time of the analysis. I analysed two small specimens (probably less pure than that examined by Faraday), which had formed in phials of the juice, with the annexed results. They were dried at 100°. The first specimen was dark brown, the second pale straw-coloured and almost transparent.

The first gave 86·1 p. c. C, 12·3 H, 0·9 ash, and 0·7 nitrogen, oxygen, and loss; the second 87·2 C, and 12·8 H.

I am anxious to call attention to the fact that the atomic constitution of caoutchouc appears to bear some simple relation to the hydrocarbons resulting from its decomposition by heat. The composition of caoutchouc coincides with that of isoprene and caoutchin, as found by analysis, to a degree which is remarkable, when we consider that caoutchouc, in addition to being non-crystalline, is scarcely capable of purification by chemical means. Additional evidence may be found in the smallness of the residue which is left on submitting caoutchouc to heat. The following results of the analyses will show the amount of confidence which may be placed in this idea :—

	Isoprene.	Caoutchin.	Caoutchouc.		
	Mean.	Mean.	Faraday.	C. G. W.*	
Carbon . .	88·0	88·1	87·2	86·9	87·3
Hydrogen .	12·1	12·0	12·8	12·4	12·1

The following table contains a summary of the physical properties of isoprene and caoutchin.

Table of the Physical Properties of Isoprene and Caoutchin.

Name.	Formula.	Boiling-point.	Specific gravity.	Vapour-density.	
				Experiment.	Calculation.
Isoprene .	$C_{10}H_8$	37° C.	0·6823 at 20° C.	2·44	2·349
Caoutchin .	$C_{20}H_{16}$	171	0·8420	4·65	4·699

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* Ash deducted.

It will be seen from what has been said upon the composition of the above bodies, that they may equally be obtained from caoutchouc or gutta percha. When the latter substance is submitted to careful distillation, the phenomena are essentially the same as with the former. The distillate contains a small quantity of water, which, instead of being alkaline, as with caoutchouc, is powerfully acid. The acid is volatile, and appears to belong to one of the lower members of the series $C_nH_nO_4$. On neutralizing the acid liquid with potash or soda, the odour of a volatile base becomes very perceptible.

The oily distillate, as with caoutchouc, consists principally of the thick uninviting fluid called by Bouchardat, *hévéène.* I have not as yet minutely examined it, but believe it to bear a polymeric relation to caoutchin.

The amount of isoprene in the crude distillate is very small, probably not more than five per cent., and, as will readily be supposed with so volatile a fluid, much is lost in the subsequent purification. It is this circumstance which has prevented me from examining it so closely as could be desired.

The caoutchin constitutes about twenty per cent. of the distillate; it was sensibly less pure than that procured from caoutchouc, and more rectifications over sodium were necessary before it was obtained in a sufficiently pure state for analysis. This partly arises from the tenacious manner in which the volatile acids above alluded to adhere to it, and render treatment with alkalies essential previous to rectification. It is also accompanied by what we are too much accustomed to vaguely term empyreumatic products. These are of a readily oxidizable nature, and may be got rid of by rectification two or three times over hydrate of potash.

The following is a brief summary of the results of the above investigation:—

1. The isolation of isoprene, $C_{10}H_8$, the existence of which among the products of the destructive distillation of caoutchouc had not been proved.

2. The production of an apparently definite oxide of the hydrocarbon $C_{10}H_8$, by the agency of ozone spontaneously generated.

3. The determination of the polymeric relation between isoprene and caoutchin.

4. The conversion of turpentine and caoutchin into the hydruret of thymyl or cymole.

5. The production of paracymole.
6. The determination of the products of the destructive distillation of gutta percha.

XXIV.—*On the Double Sulphides of Copper and Iron.*

By Frederick Field, F.R.S.E.

About two years ago, I made a verbal communication to the Chemical Society, upon certain double sulphides of copper and iron, produced by the fusion of the native compounds of those metals containing sulphur and oxygen. The experiments which were then enumerated, and which had extended at intervals over several years, have lately been resumed, and now, in a more complete form than heretofore, may perhaps be not deemed wholly uninteresting.

In countries where coal and labour are expensive, and building materials for furnaces, such as fire-bricks, fire-clay, &c., have to be economized as much as possible, it becomes necessary to devise some means in the smelting of copper ores, whereby fuel may be saved, and damage of the furnace alleviated. The process of roasting poor regulus, into a sulphide richer in copper, is that usually resorted to in England, but this roasting acts at the same time, very severely upon the sides of the furnace, as the slag, consisting to a great extent of oxide of iron, combines with the silica of the clay and of the bricks, forming silicate of iron. To avoid this difficulty, advantage is taken of the fact, that oxide and sulphide of copper mutually react upon each other, forming sulphurous acid and metallic copper—

$$2\,CuO + Cu_2S = 4\,Cu + SO_2$$

so that when an excess of the latter is employed, combined at the same time with more or less sulphide of iron, a rich regulus is produced, and the process of roasting is obviated. For example, if into a mass of fused regulus of low percentage, a few hundred weight of the carbonates of copper are introduced, and the whole brought to a state of fusion, the oxide of iron formed combines with the silica of the ore, producing a fusible slag, and a great portion of the sulphur is oxidized at the expense of the oxygen contained in the carbonates. By adopting this method, regulus of a very high percentage may be obtained, and even metallic copper, if sufficient oxygen be present in the mineral to convert the whole of the sulphur into sulphurous acid. Practically speaking, however, this latter plan is seldom or never adopted, the smelter preferring to tap the regulus when it contains from 40 to 50 per cent. of copper, as if richer, the slags invariably contain much of that metal.

Many analyses have been made of the double sulphides of copper and iron, technically known as regulus, but probably owing to the ores themselves containing many other metals, such as tin, arsenic, antimony, and occasionally silver, it can scarcely be wondered at that the results of the investigations of various chemists upon this particular subject are not very concordant. From my own experience I am led to believe, that copper regulus always has a certain definite composition, and analyses of many specimens, collected from different quarters of the world, fully confirm the idea.

It appears that the copper invariably exists in the state of disulphide (Cu_2S) in regulus, associated with iron in various states of sulphuration. The sulphides of iron seem to exist in certain relative proportions, and the richness or poverty of the regulus in copper, to depend upon the number of the equivalents of disulphide in combination with them. It cannot be denied that certain facts seem to militate against this view, as for example, the action of hydrochloric acid upon the compound. Regulus of from 25 to 50 % copper, generally evolves sulphuretted hydrogen copiously, when treated with this acid, whilst that containing from 60 to 80 % is scarcely acted upon at all; but, nevertheless, the proportions of copper, sulphur, and iron, are so invariable, as to lead us to suppose that it is the great excess of disulphide of copper, which shields or protects the sulphides of iron from the acid, rather than that those sulphides have changed their chemical condition. And this case is not without a parallel. Silver, so readily oxidized by nitric acid, is not affected by that re-agent when alloyed with an excess of gold; neither, by means of hydrochloric acid can zinc be separated from copper, when the latter is in great excess; and in like manner when the number of atoms of disulphide of copper, combined with the iron-compound are diminished, much of the iron is dissolved, which, under other circumstances, would remain unaffected. It is, therefore, evident that no results can be deduced as to the state in which the iron exists, by measuring the quantity of sulphuretted hydrogen evolved by the action of hydrochloric or sulphuric acid.

When regulus is repeatedly roasted, and the slag which accumulates upon the surface is skimmed off, a point is arrived at, when all the iron is withdrawn, and a pure disulphide of copper remains, having exactly the same specific gravity, physical appearance, and chemical composition, as the native disulphide, copper-glance. The sulphides of iron are all decomposed before the sulphide of copper is attacked, and it would almost appear that this compound plays the part of a base, as regards the sulphides of iron, and that the more concentrated the regulus becomes, the more basic is its composition. If a small quantity of oxide or carbonate of copper be dropped into a fused mass of the sulphide of iron, a disulphide of copper is produced, exercising a certain influence upon the whole compound with regard to the solvent action of acids.

Regulus appears to me to consist of one atom of sesquisulphide of iron Fe_2S_3, one atom of protosulphide FeS, and two atoms of disulphide Fe_2S, associated with disulphide of copper. Thus, a portion of clean regulus from a furnace yielded on analysis—

Copper	36·12
Iron	36·78
Sulphur	27·08
	99·98

or $(3\,Cu_2S)\,Fe_2S_3,\ FeS,\ 2\,Fe_2S$. On roasting this compound for some hours, the regulus yielded—

Copper	49·71
Iron	25·34
Sulphur	24·85
	99·90

or $(6\,Cu_2S)\,Fe_2S_3,\ FeS,\ 2\,Fe_2S$.

Again, after further roasting and skimming, another sample was subjected to analysis, and the results were as follows:—

Copper	61·34
Iron	15·61
Sulphur	22·90
	99·85

or $(12\,Cu_2S)\,Fe_2S_3,\ FeS,\ 2\,Fe_2S_3$.

Although the native yellow copper pyrites has a different composition, the blue sulphides seem to follow the same law, as the artificially prepared regulus. Thus a very pure specimen yielded me—

Copper	54·21
Iron..	21·43
Sulphur	24·12
	99·76

or $(8\,Cu_2S)\ Fe_2S_3,\ FeS,\ 2\,Fe_2S,$

which requires—

Copper	54·93
Iron	21·04
Sulphur	24·03
	100·00

It is interesting to observe the rapid decrease in the proportion of iron, in comparison with the sulphur, as the copper augments. When the regulus contains 36 % of the latter metal, it contains also 36 % iron, and about 27 % sulphur. At 50 % of copper, the sulphur and iron are in nearly equal proportions. At 60 % the iron is reduced to 16·5 %; and the sulphur to 23 %, while at 80 % copper, all the iron has disappeared, and 20 per cent. of sulphur remains.

In the appended table, a tabular form of the theoretical construction of regulus is given, as well as the results of some experiments. It will be observed on examination, that the practical results agree very closely with the theoretical numbers, from which it certainly seems probable, to say the least, that these compounds have a definite constitution, and are not accidental admixtures, as is generally maintained.

COMPOSITION of the Double Sulphides of Copper and Iron.

	CALCULATED.			EXPERIMENT.			
	Copper.	Iron.	Sulphur.	Copper.	Iron.	Sulphur.	
$(Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	17·20	52·68	30·10	....	....	....	.. ..
$(2 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	28·09	43·36	28·32	....	....	....	.. ..
$(3 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	36·09	36·84	27·06	36·12	36·78	27·08	.. ..
$(4 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	41·83	32·02	26·14	....	....	....	.. ..
$(5 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	46·24	28·32	25·43	46·34	28·19	25·27	.. ..
$(6 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	49·74	25·38	24·86	49·71	25·34	24·85	.. ..
$(7 Cu_2S) Fe_2S_3, FeS, 1 Fe_2S$	52·57	23·00	24·41	52·48	22·89	24·32	.. ..
$(8 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	54·93	21·02	24·03	54·21	21·13	24·12	Native blue Sulphide.
$(9 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	56·91	19·36	23·71	....	....	....	.. ..
$(10 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	58·60	17·94	23·44	....	....	....	.. ..
$(11 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	60·07	16·72	23 20	....	....	....	.. ..
$(12 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	61·34	15·65	23·00	61·34	15·61	22·90	.. ..
$(13 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	62·46	14·71	22·82	....	....	....	.. ..
$(14 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	63·45	13·88	22·65	....	....	....	.. ..
$(15 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	64·34	13·13	22·52	....	....	....	.. ..
$(16 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	65·14	12·46	22·38	....	....	....	.. ..
$(17 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S$	65·84	11·86	22 27	....	....	....	.. ..

XXV.—*On the Hydrocarbons produced by Destructive Distillation of Boghead Coal.*

By C. Greville Williams.

It is well known that when Frankland's and Kolbe's admirable researches on the organic radicals were first published, the formulæ adopted assumed those bodies to possess a condensation to two volumes.[*] M.M. Laurent and Gerhardt, in accordance with their system, considered themselves justified in doubling Frankland's formulæ, thus making the condensation of the radicals the same as that of the hydrocarbons generally, viz., to four volumes. But this appearing to remove from methyl and ethyl the characters of radicals in the electro-chemical sense of the term, they preferred to regard them as homologues of marsh-gas.

The progress of science showed, however, that although Laurent and Gerhardt were justified in doubling the formulæ, it was going too far to refuse the bodies in question the position of radicals: for Brodie and others have conclusively proved the derivation of these bodies from a double molecule of hydrogen. It was reserved for M. Wurtz to show that each molecule might be replaced by a different group, and thus to place the vapour-volume of the radicals altogether beyond dispute.[†]

The marsh-gas family, closely allied to the radicals in character, and belonging to the same type, are peculiarly liable to be confounded with them. The difficulty is moreover increased from the fact, that each alternate homologue of marsh-gas is isomeric with one of the radicals. This will become plain on inspection of the following table:—

Marsh-gas series.		Methyl (*radical*) series.	
Hydride of Methyl	$C_2 H_4$		
„ Ethyl	$C_4 H_6$	Methyl	$C_4 H_6$
„ Propyl	$C_6 H_8$		
„ Butyl	$C_8 H_{10}$	Ethyl	$C_8 H_{10}$
„ Amyl	$C_{10} H_{12}$		

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[*] In order to preserve uniformity between this and the previous papers on the same subject, I use the old notation, $O = 8$ and $2\,HO = 4$ vols.

[†] Ann. Ch. Phys. [3], xliv, 275.

Marsh-gas series.			Methyl (*radical*) series.	
Hydride of	Caproyl	$C_{12}H_{14}$	Propyl	$C_{12}H_{14}$
,,	Œnanthyl	$C_{14}H_{16}$		
,,	Capryl	$C_{16}H_{18}$	Butyl	$C_{16}H_{18}$
,,	Pelargonyl	$C_{18}H_{20}$		
,,	Rutyl	$C_{20}H_{22}$	Amyl	$C_{20}H_{22}$
,,	Euodyl	$C_{22}H_{24}$		
,,	Lauryl	$C_{24}H_{26}$	Caproyl	$C_{24}H_{26}$

While endeavouring to get a clue to the true nature of the indifferent hydrocarbons from Boghead naphtha, I was naturally led to pay particular attention to Dr. Hofmann's experiments on the action of heat upon valerianic acid. They were considered to prove the hydrides of the radicals high up in the series to be unable to endure a red heat: for he says,—"It appears that this term (C_8H_{10}) unable to exist at the prevailing temperature, is broken up into the more stable compounds of the series, C_nH_n, the excess of hydrogen being eliminated either in the form of marsh-gas, or as water formed by the reduction of carbonic acid to carbonic oxide;" and again,—"The members of this series appear to be far less stable than the hydrocarbons containing an equal number of carbon and hydrogen-equivalents." Further, "The instability of these substances would also explain why we have not hitherto obtained a member of the marsh-gas series, derived from the fatty acids in the various tars and naphthas which have been examined."*

It is curious to observe that while Dr. Hofmann, at the time of writing the paper alluded to, regarded bodies of the marsh-gas class, as high up even as C_8H_{10}, as unable to exist at a red heat, Frankland† had previously stated his belief that hydride of amyl would be found to exist among the products of the destructive distillation of wood and coal at carefully regulated temperatures. The paragraph is as follows;—"It is not impossible, that by regulating the temperature at which the destructive distillation of wood and coal is carried on, considerable quantities of hydruret of amyl might be cheaply obtained, which, as illuminating material, would surpass almost every other in convenience and brilliancy."

In my investigation "On some of the Products of the Destructive Distillation of Boghead Coal."‡ I showed the naphtha produced by distilling boghead coal at low temperature to be a mixture of three classes of hydrocarbons, viz., homologues of benzole, of olefiant gas, and a series having the ultimate composition, boiling points, and density, both in the fluid and gaseous states, of the radicals of the alcohols. I stated, however, that they might also be regarded as the isomeric hydrides. The inertness of the bodies in question, and the absence of all reactions, allowed no crucial experiment to be made; nevertheless their physical properties so exactly corresponded with the radicals, that it was difficult to regard them as being merely isomers. This will appear evident on reference to the annexed table, extracted from my first paper on Boghead Naphtha :—

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* Chem. Soc. Qu. J., iii, 123. † Ibid, p. 43.

‡ Philosophical Transactions, 1857.

Comparative Table of the Physical Properties of the Radicals with the Hydrocarbons from Boghead Naphtha.

Radicals.	Boiling-Points.					Densities.				Vapour-Densities.				
	Frankland.	Kolbe.	Wurtz.	Brazier and Gossleth.	C. G. Williams.	Frankland, at 11°.	Kolbe, at 18°.	Wurtz, at 0°.	C. G. Williams, at 18°.	Frankland.	Kolbe.	Wurtz.	G. C. Williams.	Theory.
Propyl $C^{12} H^{14}$	...	...	...	...	Mean. 68°	...	...	...	0·6745	...	...	...	2 96	2·97
Butyl $C^{16} H^{18}$	...	108°	106°	...	119°	...	0·6940	0·7057	0·6945	...	4 053	4·07	3·88	3·94
Amyl $C^{20} H^{22}$	155°	...	158°	...	159°	0 7704	...	0·7413	0·7365	4·899	...	4 956	4·93	4·91
Caproyl $C^{24} H^{26}$	...	...	202°	202°	202°	...	...	0·7574	0·7568	...	...	5 983	5·83	5·87

It will be observed that the only discrepancy of any moment is in the case of butyl, or hydride of capryl, the boiling point of which is 12° C. too high. This fact (which I was at first inclined to attribute to insufficient purification) induced me to spare no pains in determining the boiling point of the substance alluded to. The plan adopted being fully described in the original paper, need not be detailed here. It is necessary to state, however, that no amount of purification was found capable of reducing the boiling point below 119° centigrade.

Dürre, of Magdeburg,* repeated my experiments with great care on a naphtha of similar properties to that examined by me, but derived from brown coal, and the boiling point of the hydrocarbon of the formula $C_{16}H_{18}$ differed by only half a degree centigrade from that found by me.

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* Edinburgh New Philosophical Journal, October 1859.

The above experiments were, however, quite insufficient to determine so delicate a point as that in view, in the absence of all decisive reactions, and it seemed almost impossible for merely isomeric bodies to possess properties so nearly identical. Moreover, it is quite plain, that as bodies so closely allied to the alcoholic radicals as the olefiants and the hydrides of the positive radicals, are formed during destructive distillation, there is no obvious reason why the radicals themselves, formed as they are on the same type, and being products of the decomposition of the hydriodic ethers, should not be produced under the same circumstances.

It struck me, however, that some light might be thrown upon the question by ascertaining whether the tar from Boghead coal contained a hydrocarbon unacted upon by acids, and distilling at a lower temperature than the substance provisionally termed propyl; it being evident, that as ethyl is a gas, a mixture of the true radicals should not contain a fluid boiling below propyl.

I have succeeded in obtaining a little Boghead naphtha of sufficient volatility to enable me to try this experiment. After purification by the method described in my previous paper, a liquid was obtained boiling between 30° and 40° centigrade.

0·1636 gramme gave 0·4990 carbonic acid, and 0·2460 water—

	Experiment.	Calculation.		
Carbon . .	83·2	C^{10}	60	83·3
Hydrogen . .	16·7	H^{12}	12	16·7
			72	100·0

The vapour-density determined by Gay Lussac's method, gave the annexed result:—

Atmospheric pressure . . .	762	m.m.
Pressing column of oil reduced to millimetres of mercury . .	22·3	
Difference of level	60·0	
Temperature of vapour . . .	102°	cent.
Volume of Vapour	48·0	c.c
Weight of substance . . .	0·1110	gramme.

The formula $C_{10}H_{12}$ = 4 volumes requires:—

10 volumes carbon-vapour . $0{\cdot}8290 \cdot 10 = 8{\cdot}2900$

24 volumes hydrogen . . $0{\cdot}0692 \cdot 24 = 1{\cdot}6608$

$$\frac{9{\cdot}9508}{4} = 2{\cdot}48395$$

Experiment.	Theory $C_{10}H_{12}$ = 4 vols.
2·575	2·484

It is evident from the above numbers, that the most volatile portion of Boghead naphtha contains a considerable quantity of hydride of amyl, and in all probability, therefore, the indifferent hydrocarbons are homologues of marsh-gas, and only isomeric with the true alcohol-radicals. It is evident that the formula of hydride of amyl corresponds to certain compound radicals; this is a question upon which we are not, at present, in a position to speculate.

I have found that the hydriodic ethers, and consequently the true radicals and their innumerable derivatives, may be produced from the above hydrides by a tolerably simple series of operations. On passing through a red-hot tube, the liquid hydrides are converted into olefiants of lower formula, with evolution of several gaseous products. The olefiants, by cohobation with fuming hydriodic acid, yield the hydriodic ethers thus:—

$$\underbrace{C_nH_n + H\,I}_{\text{Olefiant.}} = \underbrace{C_nH_{n+1},\,I}_{\text{Hydriodic ether.}}$$

The process, although theoretically and practically simple enough, involves such a loss of material, that it will probably be some time before the investigation I am making upon it will be concluded. I had some hopes that the radicals and the hydrides would behave differently under the influence of heat, so as to enable me to distinguish between them by this means. The experiments as yet made in this direction appear to indicate, that, as in every other case known at present, they break up into nearly, if not absolutely, the same products.

XXVI.—*On the Synthesis of Succinic and Pyrotartaric Acids.*

By MAXWELL SIMPSON, M.B.,

[Abstracted from the Philosophical Transactions, 1860, p. 61.]

SUCCINIC acid bears the same relation to the diatomic alcohol glycol, that propionic acid bears to ordinary alcohol. Propionic acid can be obtained by treating the cyanide of the alcohol-radical with potash. Can succinic acid be obtained by treating the cyanide of the glycol-radical with the same reagent? or is it an isomeric acid that is formed under those circumstances?

$$\underbrace{C_4H_5Cy}_{\text{Cyanide of Ethyle.}} + O_2\left\{\begin{matrix}K\\H\end{matrix}\right. + 2HO = \underbrace{O_2\left\{\begin{matrix}C_6H_5O_2\\K\end{matrix}\right.}_{\text{Propionate of Potash.}} + NH_3$$

$$\underbrace{C_4H_4Cy_2}_{\text{Cyanide of Ethylene.}} + 2\left\{O_2\left\{\begin{matrix}K\\H\end{matrix}\right.\right. + 4HO = \underbrace{O_4\left\{\begin{matrix}C_8H_4O_4\\K_2\end{matrix}\right.}_{\text{Succinate of Potash?}} + 2NH_3$$

The following experiments were performed with the view of determining this point.

Preparation of Cyanide of Ethylene.

This body was obtained by submitting bromide of ethylene to the action of cyanide of potassium. A mixture of two equivalents of the cyanide and one of the bromide, together with a considerable quantity of alcohol, was exposed in well-corked soda-water bottles to the temperature of a water-bath for about sixteen hours. To prevent the caking of the salt, it is advisable to have some coarsely powdered glass in the bottles, and to agitate them occasionally. At the expiration of this time, the bottles were opened, and the alcohol separated and distilled. A semifluid residue was thus obtained, which was filtered at 100° C. It was very dark in colour, owing to the presence of a considerable quantity of a tarry matter, which was ultimately removed by exposing the residue to a powerful freezing mixture, and pressing it, while in the mixture, between folds of bibulous paper, as long as the paper was stained. After this treatment, there remained a crystalline mass, which was almost white. This was finally washed with a small quantity of ether, and dissolved in the same liquid. The residue obtained on evaporating the ethereal solution is the body in question. Dried at 100° C., it gave by analysis, numbers agreeing with the formula $C_4H_4Cy_2$.

This is, I believe, the first example of a diatomic cyanide. It has the following properties :—Below the temperature of 37° C. it is a crystalline solid of a light-brown colour, above that temperature it is a fluid oil. It cannot be distilled. Nevertheless it bears a tolerably high temperature without suffering much decomposition. Its specific gravity at 45° C. is 1·023. It is very soluble in water and alcohol, and sparingly soluble in ether. It has an acrid disagreeable taste. It is neutral to test-paper. Gently warmed with potassium, it is decomposed, cyanide of potassium being formed in large quantity. Its solution in water is not precipitated by nitrate of silver.

Action of Potash on Cyanide of Ethylene. Formation of Succinic Acid.

An alcoholic solution of crude cyanide of ethylene was prepared in the manner already described, and introduced, together with some sticks of caustic potash, into a large balloon with a reversed Liebig's condenser attached to it. Heat was then applied by means of a water-bath, which caused torrents of ammonia to be evolved. As soon as the evolution of this gas had ceased, the alcohol was distilled off, and in order to secure the complete decomposition of the cyanide, the residue was treated with a solution of potash, and exposed to heat as long as the slightest evolution of ammonia could be detected. A considerable excess of strong nitric acid was then cautiously added, and the whole evaporated to dryness. The nitric acid destroys all the impurities present, and leaves a mixture of nitrate of potash and a free acid, easily separable by means of alcohol, which dissolves the latter but not the former. The acid obtained, on distilling off the alcohol, was twice crystallized from water, dried at 100° C., and analysed. The numbers obtained agreed perfectly with the formula of succinic acid $C_8H_6O_8$.

A silver-salt* was also prepared and analysed. It gave 63·87 p.c. silver, and 14·49 carbon, instead of 65·06 of the former, and 14·46 of the latter, as required by the formula $C_8 H_4 Ag_2 O_8$.

The acid possessed also all the properties of succinic acid. It melted a few degrees above 180° C., and sublimed on the application of a higher temperature. It was very soluble in water and alcohol, and sparingly soluble in ether. It gave when neutralized, a reddish-brown precipitate with sesquichloride of iron. Moreover on digesting this precipitate with amonia, and filtering, an acid could be detected in the filtered liquor, which gave white precipitates with nitrate of silver, and with a mixture of chloride of barium and alcohol. On passing a stream of hydrochloric acid gas through a solution of the acid in absolute alcohol, an oil insoluble in water was obtained, which distilled between 220° and 225° C. This was evidently succinic ether.

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* The acid from which this salt was prepared was obtained in a somewhat different manner. Instead of liberating it from its combination with potash by means of nitric acid, hydrochloric was employed. The whole was then evaporated by a gentle heat, and the residue repeatedly digested with absolute alcohol. On evaporating the alcohol, the succinic acid was obtained free from the chloride of potassium which accompanied it. The silver-salt evidently contained a trace of an acid having a higher atomic weight than succinic acid.

The above is an easy and a productive process, and yields the acid at once in a state of purity. From 1,500 grains of bromide of ethylene, I obtained 480 grains of succinic acid, or nearly 33 per cent.

I have studied, in addition, the action of some acids and of nitrate of silver on cyanide of ethylene.

Action of Nitric Acid on Cyanide of Ethylene.

When cyanide of ethylene and nitric acid are evaporated together on a water-bath, a white crystalline mass is obtained. This proved to be a mixture of succinic acid and nitrate of ammonia. The acid can be completely separated from the nitrate by means of ether, of which, however, a large quantity is requisite A silver-salt of the acid was prepared and analysed. It gave 64·07 instead of 65·06 per cent. of silver.

Action of Hydrochloric Acid on Cyanide of Ethylene.

A mixture of cyanide of ethylene and an excess of strong hydrochloric acid was exposed for a few hours in a sealed tube to the temperature of 100° C. On cooling, the contents of the tube became a mass of crystals, which were ascertained to be a mixture of succinic acid and chloride of ammonia. The following equation will explain the reaction :—

$$C_4H_4Cy_2 + 2HCl + 8HO = C_8H_6O_8 + 2NH_4Cl$$

This reaction enabled me to determine the amount of nitrogen in the cyanide of ethylene in a very easy manner. It was simply necessary to perform the above experiment on a weighed quantity of the cyanide, and afterwards to ascertain the amount of nitrogen in the mixed crystals by means of bichloride of platinum in the usual way.

Action of Nitrate of Silver on Cyanide of Ethylene.

About three equivalents of crystallized nitrate of silver were rubbed up in a mortar with one equivalent of pure cyanide of ethylene and a considerable quantity of ether. The ether was then poured off, and the residual salt dissolved in boiling alcohol. On cooling, the alcohol became a mass of brilliant pearly plates. These were washed with ether, dried at 100° C., and analysed. The numbers obtained led to the formula $C_4H_4Cy_2 + 4\ (AgO.\ NO_5)$.

That this body is simply formed by a union of the cyanide and nitrate in these proportions without decomposition, is confirmed by the fact that, when the crystals are treated with strong hydrochloric acid and the whole evaporated on a water bath, succinic acid can be detected in the residue. The acid is evidently formed by the action of the liberated nitric acid on the cyanide of ethylene. The crystals are soluble in water and alcohol, but insoluble in ether. When heated they explode like gunpowder. They do not, however, detonate on percussion. This compound may possibly throw some light on the constitution of the fulminates. When treated with nitrous acid (NO_3), it gives a remarkable silver-salt, which is insoluble in alcohol, and so fusible, that it can be melted under that liquid.

I have endeavoured to substitute two equivalents of bromine for the two of cyanogen in the cyanide of ethylene, so as to regenerate bromide of ethylene, but without success, the molecule being completely broken up by the action of the bromine.

We are now in a condition to answer the question proposed at the commencement of this paper. Succinic acid *can* be obtained from glycol in the same manner as propionic acid from ordinary alcohol, the bromide of ethylene, the point from which I started being capable of derivation from the diatomic alcohol.

We are now enabled, thanks to the researches of Messrs. Perkin and Duppa, and of M. Kekulé*, to build up three highly complex organic acids (succinic, paratartaric, and malic) from a simple hydrocarbon; and what is more important, we are enabled to do this by processes, every stage of which is perfectly intelligible.

The question now arises: Is the foregoing reaction capable of general application? Can the homologues of succinic acid be obtained in a similar manner? With the view of determining this point, I have endeavoured to prepare pyrotartaric acid from the cyanide of propylene, the radical of propyl-glycol.

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* Quarterly Journal of the Chemical Society, July, 1860; and Bulletin de la Société Chimique de Paris, 10 Août, 1860, p. 208.

Preparation of Cyanide of Propylene.

This body, which forms the first step in my process for pyrotartaric acid, I succeeded in obtaining in the following manner:—A mixture of one equivalent of bromide of propylene and two of cyanide of potassium, together with a considerable quantity of alcohol, was exposed to the temperature of a water-bath in well-corked soda-water bottles for about sixteen hours. Their contents were then filtered, and the alcohol distilled off the filtered liquor. A liquid residue was thus obtained, which was very black, and by no means of a promising appearance. This was filtered at 100° C., and digested with ether, which left a large quantity of a black tarry matter undissolved. The residue obtained on evaporating the ethereal solution was then submitted to distillation. Almost all the liquid passed over between 265° and 290° C. The fraction distilling between 277° and 290° gave, by analysis, numbers agreeing approximately with the formula $C_{10}H_6N_2$.

I do not think it possible to obtain this body in a state of purity, unless by fractional distillation *in vacuo*, since it suffers partial decomposition when distilled in air, as evidenced by a slight evolution of ammonia during the process.

The properties of this cyanide very much resemble those of the preceding. It differs however in its physical state, which is that of a liquid at the ordinary temperature of the air. It is soluble in water, alcohol, and ether; has an acrid taste; is colourless and neutral to test-paper. It is decomposed with great facility by potassium, cyanide of potassium being formed in large quantity. Its solution in water gives no precipitate with nitrate of silver. Heated with potash, it forms an acid and gives off ammonia.

Formation of Pyrotartaric Acid.

A mixture of one volume of cyanide of propylene, distilling between 265° and 290° C., and about 1½ volume of strong hydrochloric acid, was exposed in a glass tube hermetically sealed to the temperature of a water-bath for about six hours. Long before the expiration of this time, the contents of the tube had become a mass of crystals. These were dried at 100° C., and dissolved in absolute alcohol. The residue obtained on evaporating the alcoholic solution was then twice crystallized from water, and finally dissolved in ether, in order to remove the last traces of the ammoniacal salt formed in the process. The body obtained on distilling off the ether is the acid in question. Dried at 100° C. it gave, by analysis, numbers corresponding with the formula of pyrotartaric acid.

It had also all the properties ascribed to this acid by Pelouze and Arppe. The crystals were colourless and very soluble in water, alcohol and ether. It had an agreeable acid taste, and expelled carbonic acid from its combinations with the alkalies. It became semifluid at 100° C., and melted completely a few degrees above that temperature. Long-continued ebullition in a glass tube converted it into an oil, which was insoluble in cold water, and no longer affected litmus paper, but gradually dissolved in boiling water, recovering at the same time its acid reaction. Lime-water was not affected by a solution of this acid. Neutralized by ammonia, it gave a white curdy precipitate with nitrate of silver. Acetate of lead caused no precipitate with the neutralized acid. On the addition, however, of alcohol to the mixed solutions, a bulky white precipitate was obtained, which melted into oily drops on heating the liquid in which it was suspended. The following equation will explain the reaction which gives rise to this acid:—

$$C_6H_6Cy_2 + 2HCl + 8HO = C_{10}H_8O_8 + 2NH_4Cl.$$

Pyrotartaric acid bears the same relation to propyl-glycol that butyric acid bears to propylic alcohol:—

$$\underbrace{C_6H_8O_4}_{\text{Propyl-glycol.}} \qquad\qquad \underbrace{C_6H_8O_2}_{\text{Propylic Alcohol.}}$$

$$\underbrace{C_{10}H_8O_8}_{\text{Pyrotartaric Acid.}} \qquad\qquad \underbrace{C_8H_8O_4}_{\text{Butyric Acid.}}$$

The claims of this acid to be considered as the homologue of succinic acid, which some chemists do not recognize, are now, I think, fairly established, seeing that these two acids can be obtained by similar processes from homologous hydrocarbons.

The foregoing reaction, which, I think, we may now look upon as capable of general application, will no doubt place in our hands some of the missing acids of the succinic series.

It is highly probable that there exists a series of isomeric acids running parallel to these, which may be obtained by similar processes from the diatomic radicals contained in the aldehydes. Thus from the cyanide of ethylidene ($C_4H_4Cy_2$) we may hope to get an isomer of succinic acid.

The reactions just described lend, I think, some support to Frankland and Kolbe's view of the constitution of these acids, namely, that they are composed of two equivalents of carbonic acid, in which two equivalents of oxygen are replaced by a diatomic radical. However this may be, it is convenient, at all events, to formulate these bodies according to the carbonic acid type:—

$$\underbrace{2HO,\ C_4H''_4\begin{pmatrix}C_2O_2\\C_2O_2\end{pmatrix}O_2}_{\text{Succinic Acid.}} \qquad \underbrace{2HO,\ C_6H_6''\begin{pmatrix}C_2O_2\\C_2O_2\end{pmatrix}O_2}_{\text{Pyrotartaric Acid.}}$$

I propose to continue my researches in this direction, and to extend them to the cyanides of the triatomic radicals.

XXVII.—*On the transformations of Citric, Butyric, and Valerianic Acids, with reference to the artificial production of Succinic Acid.*

By Dr. T. L. Phipson,

[Abstract.]

The author's experiments confirm the result formerly obtained by How and by Dessaignes, that citrate of lime fermented in contact with putrefying casein, yields butyric but not succinic acid. Now as malic acid, which has nearly the same composition as citric acid, has been shown by Dessaignes to yield, under similar circumstances, first succinic and then butyric acid, it appeared not improbable that citric acid might also, by certain modifications of the conditions of the decomposition, be made to yield succinic acid.

Citrate of soda, mixed with a considerable quantity of carbonate was therefore fermented for some weeks with uncooked putrid beef; the products obtained were butyric acid, a compound which imparted a peculiar odour to the liquid, and carbonic acid which converted the carbonate of soda into bicarbonate:

$$\underset{\text{Citric Acid.}}{C_{12}H_8O_{14}} = \underset{\text{Butyric Acid.}}{C_8H_8O_4} + 4CO_2 + O_2$$

but no succinic acid.

Citrate of lime, however, fermented with a small quantity of boiled beef, yielded butyric acid and a small quantity of succinic acid.

Citric acid oxidised by permangate of potash at a temperature a little above summer-heat, was found to yield nothing but oxalic acid :

$$\underset{\text{Citric Acid.}}{C_{12}H_8O_{14}} + O_{12} = \underset{\text{Oxalic Acid.}}{3C_4H_2O_8} + 2HO.$$

Butyrate of lime oxidised by permanganate of potash at a temperature a little below the boiling point of the liquid, yielded succinic acid and acetic acid :

$$2C_8H_8O_4 + O_{10} = C_8H_6O_8 + 2C_4H_4O_4 + 2HO.$$

The acetic acid unites with the butyric acid to form butyro-acetic acid, a compound which obstinately resists the ordinary action of the permanganate. Nevertheless, the conversion of butyric acid into succinic acid in this manner, was found to be much more rapid than by oxidation with nitric acid, the process formerly pointed out by Dessaignes.

Valerianic acid treated with permanganate of potash yields, in like manner, succinic acid and aceto-valerianic acid.

The ethyl-compounds of butyric and valerianic acids are oxidised by the permanganate more quickly than the acids themselves.

The author considers it probable also that suberic acid may be formed in small quantity in these reactions.

XXVIII.—*On a mode of taking the Vapour-density of Volatile Liquids at temperatures below the boiling point.*

By Dr. Lyon Playfair, C.B., F.R.S., and
J. A. Wanklyn, F.R.S.E.

[Abstracted from the transactions of the Royal Society of Edinburgh, Vol. XXII., Part III.]*

It is commonly said that vapour-densities taken at high temperatures are more correct than those taken at low temperatures.

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* This abstract has been revised by the Authors, who have added some additional matter.

A more accurate statement of the case is—vapour-densities taken at a distance from the point of liquefaction are more correct than those taken near that point.

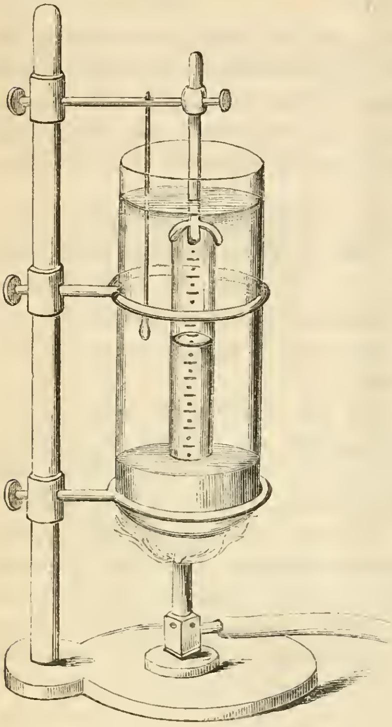
When a vapour approaches the point at which it passes into the liquid state, it loses some of the characteristics of a true gas, it ceases to expand quite uniformly for equal increments of heat, and it manifests a tendency to condense on the sides of the containing vessel. Either of these properties would make the determination of a vapour-density abnormal.

We are, however, inclined to believe that the effects upon the density, which are really due to these causes, have been exaggerated. The examples about to be brought forward show that only a moderate distance (measured either in temperature or in pressure) from the point of liquefaction is enough to render the density of a vapour nearly normal.

We believe that, in the few cases where any great difference is found between a vapour-density taken at a point moderately removed from the point of liquefaction, and one taken at a point far removed from the point of liquefaction, there is a chemical and not a merely physical change. Thus we hold that sulphur-vapour has sometimes one and sometimes another chemical formula, according as it is more or less heated. Peroxide of nitrogen, which we shall show has two radically distinct densities at high and low temperatures, has the composition N_2O_8, at ordinary temperatures and NO_4 at the temperature of boiling water.

A vapour may be removed from its point of liquefaction, either by raising its temperature, or by diminishing the pressure upon it, or by adding a certain quantity of a permanent gas to dilute it. If it be required to take a vapour-density at a low temperature, the vapour must be removed from its point of liquefaction by one or other of the latter methods. We propose to introduce the employment of the last-named method, to mix vapours with permanent gases instead of lowering the barometric pressure. We shall point out as we proceed, the practical advantages which the method of dilution has over the method of directly diminishing the barometric pressure. Here we bring forward experiments to prove that such dilution is really effective in rendering the density of vapours normal.

For this part of the enquiry, a slight modification of Gay Lussac's method of determining vapour-densities was found to be most convenient. A carefully dried graduated tube is filled with warm mercury, and inverted in the mercurial trough. Next, dry hydrogen is introduced. The gas is then measured, adopting the precautions which are requisite in measurements for a gas analysis. The liquid to be operated upon, of which a weighed portion is contained in a small glass bulb, is subsequently passed up to the hydrogen contained in the graduated tube. The tube, with its contents, is then lifted out of the mercurial trough by means of a small iron cup, and transferred to the bath in which it is to be heated, and which contains some mercury, occupying about an inch of its interior. An adjustment of the graduated tube having been made, water is poured into the bath, and heat applied, until the boiling-point of the liquid under examination has been passed. After all the liquid contained in the bulb has evaporated, the bath is allowed to cool very slowly, being stirred up constantly, so as to keep its temperature uniform throughout. Before each observation, great care was taken to ensure uniformity of temperature.



The following minute corrections were made:—

1. A correction for meniscus equal 0·3 cubic centimeter.

2. A correction for expansion of the glass tube, which amounts to from ·40 cubic centimeter to 0·1 cubic centimeter.

Both the barometric column and the mercurial column contained in the graduated tube were reduced to zero, according to tables given for that purpose in Bunsen's "Gasometry." The water column occupying the bath was measured in millimeters, corrected for temperature, and reduced to mercurial measure.

Series of Experiments with Slightly Moist Alcohol.

	Observed volume in Cub. Centimeters.	TemperatureC.	Pressure in Millimeters.	Vol. in Cub. Cent. corrected at 0° C. and 760 m.m. Pressure.
Dry Hydrogen	68·18	7° C.	600	52·482
Dry Hydrogen and Alcohol Vapour—Observation 1,	130·94	101°	732·9	92·189
Dry Hydrogen and Alcohol Vapour—Obs. 2, ..	126·04	84°	724·6	91·916
Dry Hydrogen and Alcohol Vapour—Obs. 3, ..	124·28	77·5°	720·9	91·840
Dry Hydrogen and Alcohol Vapour—Obs. 4, ..	122·68	70·5	717·9	92·117
Dry Hydrogen and Alcohol Vapour—Obs. 5, ..	120·02	61°	712	91·922

The numbers contained in the last column are obtained from those in the other columns, by applying Marriotte's law, and using the coefficient ·00366 for the expansion of 1° C. Inspection will show that the pressures are nearly alike in the five observations made of hydrogen mixed with alcohol-vapour, whilst the temperatures vary 40° C.

Since the numbers in the last column are almost identical, it follows that the coefficient of expansion adopted in their calculation is correct.

The alcohol in this instance was supposed to have been dry, but subsequent examination showed that a small quantity of water had escaped the action of the dehydrating agents. The vapour-density of this moist alcohol may be found by the following calculation. We will take Observation 1:—

	Cubic cent.
Vol. of hydrogen + alcohol vapour	= 92·189
Vol. of hydrogen	= 52·482
	39·707

The weight of the alcohol which was introduced was ·0775 grm.
Therefore, 39·707 cub. cent. of alcohol vapour weigh ·0775 grm.
39·707 cubic cent. of air weigh ·05137 grm.

$$\frac{\cdot 0775}{\cdot 05137} = 1\cdot 508, \text{ the vapour-density of the moist alcohol.}$$

If the other observations be calculated, the numbers will be found to differ very little from that obtained from the first; indeed Observation 3rd, which departs furthest from Observation 1st, gives for the vapour-density the quantity 1·522.

The same sample of moist alcohol was made the subject of an experiment, in which its vapour-density was determined in the usual way, without the employment of a permanent gas:—

The results were:—

Temperature.	Vapour-density.
95°	1·551
83°	1·565

In the first described experiment, where hydrogen was present, we found the vapour-density of the alcohol to lie between 1·508 and 1·522. It would appear, therefore, that the presence of hydrogen lowers the density of alcohol vapour; the lowering cannot be due to difference of pressure; for in the experiment where the higher vapour-density was obtained, the pressure was about 630 millimeters, whilst in the other experiment it was about 730.

Experiments on perfectly Anhydrous Alcohol.

Weight of the Alcohol taken = ·0889. grm.

	Observed volume in Cub Centimeters.	TemperatureC.	Pressure in Millimeters.	Vol. in Cubic Cent. corrected at 0° C. and 760 Millimeters.
Vol. of Dry Hydrogen ..	43·16	7°	572·07	31·676
Hydrogen and Alcohol Vapour—Observation 1, ..	110·84	99°	710·6	76·073
Hydrogen and Alcohol Vapour—Obs. 2, ...	107·16	83·5°	699·7	75·565
Hydrogen and Alcohol Vapour—Obs. 3, ...	102·74	68°	695·1	75·238

A correction of 0·4 cub. cent. for air contained in the alcohol bulb has to be made. This quantity must be subtracted from the volume of alcohol vapour.

The vapour-densities, as deduced from the three observations, are as follows :—

	Vapour-Density.
Observation 1 at 99°	1·562
„ 2 at 83·5°	1·580
„ 3 at 68°	1.592

The same sample of anhydrous alcohol gave without hydrogen :—

Temperature.	Vapour-density.
At 100·5°	1·599
At 86·5°	1·602

Here, again, we notice the same peculiarity as in the former experiments with the specimens of moist alcohol, viz., the vapour-densities taken with hydrogen are rather lower than those taken without it.

The theoretical vapour-density of alcohol calculated from the specific gravity of hydrogen is $\frac{46}{2} \times \cdot0691 = 1\cdot5893$, a number which agrees with our experiment.

In several elementary works on Organic Chemistry, in Regnault's "Manual" for example, the following vapour-densities for alcohol at different temperatures are given :—

Temperature.	Vapour-density.
88° C.	1·725
98°	1·649
110°	1·610
125°	1·603
150°	1·604
175°	1·607
200°	1·602

Our observation does not confirm the decrease of ·08 in density between 88° C. and 98° C. Between 86·5° and 100·5°, we have an decrease of ·003 only.

Experiments made in like manner with Ether which had been purified and dried with great care, gave :—

With hydrogen :—

	Temperature.	Vapour-density.
At	69·5° C.	2·499
At	20·8°	2·539

Without hydrogen:—

	Temperature.	Vapour-density.
At	94° C.	2·541
At	52° C.	2·580

The theoretical vapour-density of ether is $\frac{74}{2} \times \cdot 0691 = 2 \cdot 5567$.

These experiments show that admixture of hydrogen with the vapour of alcohol or ether renders it capable of being cooled down much below the boiling point, without losing its normal density.

Some experiments by Regnault, undertaken for meteorological purposes, have shown that the aqueous vapour suspended in the atmosphere has the normal-density 0·622. We may, therefore, regard the first question as satisfactorily answered.

But whether it is *more* effective to add a permanent gas than to diminish barometric pressure, will require a set of very careful experiments. The practical advantage of using the gas, rather than lowering the pressure, will be evident from the following considerations:

Let it be required to expand 10 cub. centimeters of a vapour to double the volume. To do so, half the barometric pressure must be taken off by means of a column of mercury between the lower level of the gas and the level of the mercury in the trough.

We thus get volume = 20 C.C.; mercurial column in the bath = ½ barometric height.

But let the expansion be made by adding an equal volume of permanent gas, and we have volume of gas and vapour = 20 C. C.; mercurial column in the bath = 0.

Thus it appears that by using a gas the long mercurial column is saved. Several other advantages attend the use of the gas; but the circumstance that the gas requires an apparatus only of the ordinary size, while to work at low pressures would require at least double the ordinary capacity of tube, bath, and everything else, is alone sufficient to make the former method much more practicable than the latter.

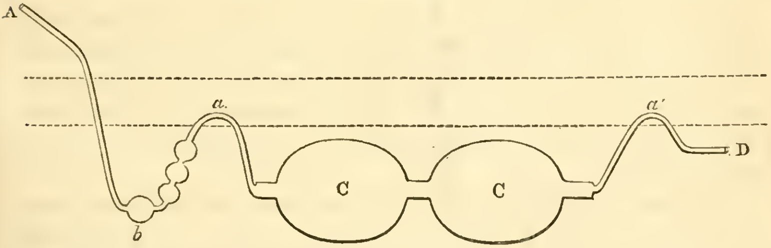
We next describe the way of proceeding when it is desirable to avoid heating the substance which is operated upon, when a degree of heat approaching that at which the substance boils would produce decomposition.

By the plan about to be described, the vapour is never heated higher than the temperature at which its density is to be taken.

The principle is that of Dumas' method—viz., the weighing of a given volume of vapour: the mode of carrying it out is, however, so different, that a minute description of the apparatus will be necessary.

Those who have occupied themselves with Dumas' mode of taking vapour-densities, will be well aware, that one of the difficulties of using it for temperatures near the boiling point of a liquid, is due to the circumstance that it is impossible to know when all the liquid has assumed the state of vapour.

Our modification of the method consists in placing the liquid to be vaporized outside of that part of the apparatus which, when hermetically sealed, will contain the vapour mixed with gas. The apparatus consists of a pair of large bulbs, connected together by means of a neck, and terminating on either side in narrow glass tubes, which are bent and blown into small bulbs, as represented in the drawing. The bulbs C and C are large, and together capable of holding from 200 to 400 cubic centimetres. The bulbs *b* are very small, being mere dilations of the narrow tube. They are to contain the liquid to be examined. The bends *a* and *a* should be on the same level, and thin, so as to admit of fusion by the lamp. Altogether the apparatus should not weigh more than 65 grm. The following mode is employed in making an experiment with the apparatus.



After being cleaned and filled with the dry air of the balance-case, the bulb-apparatus is weighed, and then transferred to the bath, being grasped by a retort-holder, which takes hold of the neck connecting the large bulbs C and C. The end A is then jointed to a hydrogen-apparatus by means of a small caoutchouc tube; the other extremity D, which projects out of the bath through an orifice in the side of that vessel, is likewise connected, by means of a caoutchouc tube, with a long narrow glass tube pointing downwards, and designed to prevent diffusion. Dry hydrogen gas is then passed through the apparatus to repletion. Whilst this is going on, warm water is poured into the bath—the hole in its side through which the extremity D passes being stopped up with putty, which makes a very convenient water-tight stopping. The addition of water is continued, until the bends *a a* are totally submerged. When the apparatus is full of hydrogen, the connection at A is interrupted, and the liquid, of which a vapour-density determination is made, introduced at A.

On re-establishing the communication with the hydrogen-apparatus, a stream of dry hydrogen passes through the dilatation *b*, and becoming more or less saturated with vapour, enters the great bulbs C and C.

No more liquid is placed in *b* than is sufficient to fill that bulb half-full, the three suplementary dilatations near *b* acting as safety-bulbs, to avoid the effects of splashing.

The temperature of the bath is raised very slowly, the water being constantly stirred, so as to ensure uniformity of temperature When the temperature is three or four degrees below the point at which a vapour-density determination is required, the current of hydrogen is nearly stopped.

The object of this is to avoid complete saturation of the gas with vapour. By this device, the greater part of the gas which is present in C and C, at the end of the operation, has entered at a lower temperature than that at which the apparatus is sealed, and, consequently, is only partially saturated at the moment of sealing the apparatus.

The desired temperature having been attained, sufficient water to expose the bends *a a*, but not the large bulbs C C, is suddenly let out of the bath, by opening a large tap situated close to the bottom of the bath. The current of hydrogen having been entirely stopped, the flame is applied to *a* and *a*, until the apparatus is sealed up in both places. The temperature of the bath having been again noted, and also the height of the barometer, the bulbs C and C which contain the vapour and hydrogen, are removed from the bath, carefully cleaned, and subsequently, along with the other two fragments (viz., the portion A to *a* and the portion *a* to D, also carefully cleaned), transferred to the balance-case and weighed.

The difference between this latter weighing and that at the beginning of the operation gives, when the weight of the displaced air is added to it, the weight of C C filled with a mixture of hydrogen and vapour at the barometric pressure and temperature of the bath at the time of sealing.

The remainder of the operation having for its object to find how much hydrogen is enclosed in C C, and also the capacity of C C, is conducted thus:—The hermetically sealed C C, is placed in cold water, and one of its sealed extremities nipped off whilst still under water, which enters and occupies the space not filled with hydrogen. After remaining in water for a number of hours, until the vapour has been completely absorbed, the apparatus is lifted vertically out of the water, care being taken not to heat the hydrogen contained in the bulbs, for which purpose a holder is employed. The temperature of the water is observed; also the height of the barometer.

The apparatus, together with the water which has thus entered, is then weighed. It is afterwards completely filled with water, and again weighed.

The difference between the weight of the bulbs empty, and filled with water, gives the total capacity of the apparatus.

The difference between the weight after the first portion of water has entered, and the weight of the apparatus quite full of water, gives the volume of the hydrogen at the temperature of the water and at the barometric pressure, minus the column of water contained in the bulbs when they are held over the water out of which they had been lifted. This column is measured after the first weighing of bulbs and water has been made.

Such is the process which we employ to take vapour-densities of bodies incapable of being heated to their boiling points without decomposition.

Exception may perhaps be taken to the mode of measuring the hydrogen included on sealing the bulbs. We will answer some objections which might naturally be raised.

It might be feared that the vapour would not be perfectly absorbed by water; but when it is considered how much water there is, and how little vapour has to be acted upon by it, it will be evident that only in those instances where the vapour is nearly insoluble in water, will there be any chance of appreciably incomplete absorption. Only in those instances where the substance is at once insoluble in water and possesses a high tension at ordinary temperatures, could error arising from this source become serious.

With regard to the absorption of hydrogen by water, it may be remarked that since between 8° and 11° C, the absorption-coefficients of hydrogen and common air, as determined by **Bunsen**, are nearly identical, the measurement of hydrogen over water is so far unobjectionable.

As an example of the method, we subjoin the particulars of a vapour-density determination of absolute alcohol, made 30° C. below its boiling point:—

Barometer (corrected to 0° C.) = 763·094 m.m.
Temperature of the balance-case, 7·5° C.
Weight of apparatus in dry air, = 69·959 grm.
Temperature at the time of sealing 48° C.
Weight of the apparatus + H + vapour = 69·5275.
Weight of apparatus + water (at 5·2° C.) = 191.76 grm.
water column, 122 m.m.
Weight of apparatus filled with water = 545·36 grm.

	Volumes corrected at 0° C, and 760 m. m. pressure, Cubic centimetres.		grm.
Hydrogen + vapour,	406·43	weighing	0·1695
Hydrogen,	341·27	,,	0·0306
	65·16		0·1389

Therefore, 65·16 cub. c. of alcohol vapour weigh ·1389 grm.
But 65·16 cub. c. of air weigh ·0843 grm.

$$\text{Vapour-density of alcohol} = \frac{\cdot 1389}{\cdot 0843} = 1{\cdot}648.$$

Two experiments made upon very small quantities of water showed results almost as near the theoretical quantity as the balance will admit. In neither case did the weight of aqueous vapour each 10 milligrammes:—

Exp. 1. Vapour-density of water = 0·671.
Exp. 2. Vapour-density of water = 0·654.

$$\text{Theoretical density of water, } \frac{18}{2} \times 0{\cdot}691 = 0.6219.$$

When **Dumas'** method of vapour-density determination is employed, the practical advantages of diluting with a gas rather than working at diminished pressures are very obvious. We may call attention to two points.

When the gas is used, in the manner described above, the sealing up of the apparatus is managed whilst there is no difference between the pressure inside and outside. Let the apparatus be connected with an air-pump, and let the attempt be made to work in vacuo, and great difficulty will be experienced in quickly sealing up at the bends of the apparatus.

Further a very thin and light glass vessel may be used when gas is employed; for when the sealed bulbs become cold, they have to withstand only a fraction of the barometric pressure; and, precisely in those cases where the lightest and largest bulbs are desirable, where the proportion of vapour to gas is the smallest, just there does it happen that the fraction of barometric pressure to be afterwards withstood is the very smallest.

Experiments upon Acetic Acid vapour.

Cahours has obtained by the usual processes;

	Temperature.	Density.
Density of acetic acid vapour at	125° C .	3·180
„ „	150 .	2·727
„ „	200 .	2·248
„ „	270 .	2·088

		Vapour-density.
The theory requires	$C_4H_4O_4$.	2·073
	$C_8H_8O_8$.	4·146

Stated in general terms, our results are :—by adding hydrogen, a vapour-density of 2·073 can be got at least as low as 150° C.; whereas at 60° C., even in spite of 16 vols. of hydrogen to one of vapour, the vapour-density of acetic acid approaches to 4·0

Instances of the employment of the foregoing methods.

Nitrate of Ethyl.—Among the nitrates, the nitrate of methyl alone has been made the subject of a vapour-density determination. Bodies of this kind become explosive on being raised only a few degrees above their boiling points, and hence are difficult to treat by the usual methods.

We have deemed it interesting to estimate the vapour-density of nitrate of ethyl.

The vapour-density determination was made by the modification of Gay-Lussac's method. The gas employed as the diluent was dry nitrogen.

The results were—

Temperature.			Vapour Densities.
at 85·5°C	..	..	3·112
,, 90°	..	..	3·094
,, 70·3°	..	..	3·065
,, 64·9°	..	..	3·079

$\left.\begin{matrix}C_4H_5\\NO_4\end{matrix}\right\}O_2$ requires $\frac{91}{2} \times \cdot0691 = 3\cdot144$, which is sufficiently near the experimental density.

Nitric Acid.—It can hardly be said that the state of condensation of the acids has been determined by direct experiment. Most of the acids are too little volatile, or suffer decomposition at temperatures too low to admit of such experiments. And those acids whose vapour-densities have been actually observed are seldom in perfect accordance with theory. The vapour-density of sulphuric acid, for example, is abnormal: and although we are far from demurring to the explanation that that acid suffers decomposition into anhydride and water, it must be allowed that direct experiment has not yet established the molecular weight indicated by the formula $\left.\begin{matrix}S_2O_4\\H_2\end{matrix}\right\}O_4$

Again, the series of fatty acids, although normal at high temperatures, are abnormal at low temperatures: indeed, it is difficult to find an example of an acid which does not offer some anomaly of the kind.

We have selected nitric acid for experiment. As will be apparent by-and-by, this acid is regular, having for its molecular weight the number answering to the formula $\left.\begin{matrix}NO_4\\H\end{matrix}\right\}O_2$

The acid employed was distilled from sulphuric acid, then from dried sulphate of copper, and lastly, warmed in a stream of dry carbonic acid, so long as its colour became less yellow. The final product was found to be quite free from sulphates and chlorides. Its strength, as indicated by alkalimetry, was satisfactory. Its colour was a very pale yellow, which the transmission of carbonic acid was incapable of rendering fainter.

From our observation, we are inclined to believe that the last yellow tinge cannot be removed from monohydrated nitric acid by warming for any length of time in a current of perfectly dry gas; but the presence of a minute trace of moisture in the transmitted gas at once decolorises the acid. The success of the employment of urea as a means of depriving nitric acid of colour, depends partly on the production of water. We need hardly remark that we avoided the use of urea. We believe, moreover, that the quantity of peroxide of nitrogen requisite to give the yellow tinge is imponderable.

As nitric acid attacks mercury, Gay-Lussac's process is quite innapplicable to it; and since nitric acid undergoes some decomposition on boiling, Dumas' process would not answer without some modification.

The following determinations have been made by the method previously described. The gas used to dilute the nitric acid vapour was dried air.

I.

Determination of Vapour-density of Nitric Acid at 68·5° *C.*

		Cubic Centimeters at 0° C. and 760 m. m.		Grm.
Vol. of Air + Vapour	=	384·60	weighing	·7255
,, Air	=	962·48	,,	·3395
		132·12		·3860

Hence 132·12 cub. cent. of nitric acid vapour weigh ·3860 grm. Vapour density = 2·258. In the above experiment the bulbs, when sealed up, were perfectly colourless.

II.

Determination of Vapour-densitg of Nitric Acid at 40·5° *C.*

	Cubic Centimeters at 0° C. and 760 m. m.		Grm.
Vol. of Air + Vapour	317·62	weighing	·4664
,, Air	286·28	,,	·0705
	31·24		·0959

Hence 31·24 C. C. of nitric acid vapour weigh ·0959 grm. Vapour density = 2.373. In this instance the bulbs were very faintly tinged with peroxide of nitrogen. Possibly this may be the real reason why in this case the number is a little higher than in the former experiment.

The results are :—

Temperature.	Vapour-densities
at 68·5°	2·258
„ 40·5	2·373

The formula $\left.\begin{matrix}NO_4\\H\end{matrix}\right\}O_2$ requires $\frac{63}{2} \times \cdot0691 = 2\cdot1766$.

It thus appears that nitric acid vapour is nearly normal, even at many degrees below the boiling point, under ordinary atmospheric pressures.

Here the remark may be made, that one of the sources of uncertainty belonging to Dumas' method is avoided. Several grammes of substances are generally taken for Dumas' vapour-density determination. Fractional distillation takes place in course of the operation, so that unless the substance be of extreme purity, the specific gravity obtained is liable to depart widely from the mean specific gravity of the sample.

The method which we have described completely avoids this. Only a small quantity of substance is necessary, and even that need not be completely evaporated, since the portion of the apparatus containing the substance is afterwards separated from the portion filled with gas and the vapour.

Peroxide of Nitrogen NO_4.—Peroxide of nitrogen offers one of the examples of physical and chemical properties in opposition. Whereas NO_4 represents Cl. (one equivalent of NO_4, replacing just as much as one equivalent of Cl), NO_4 is physically equivalent to Cl_2. The wonderful deepening in colour which peroxide of nitrogen undergoes on being heated, led us to suspect that molecular change might also occur. This expectation has been fully realised. We deduce from our experiments that peroxide of nitrogen exists in two states; that there are two bodies having the same percentage composition as peroxide of nitrogen, but which are polymeric.

The body existing at high temperatures requires the formula NO_4, that existing at low temperatures requires the formula N_2O_8.

The peroxide of nitrogen used in this research was prepared partly by distilling nitrate of lead, and partly by distilling a mixture of nitrate of lead with chloro-chromate of potash. The products from several operations were purified together, and placed in a single hermetically sealed tube. Analysis showed that it was pure.

Before proceeding to take the specific gravity of peroxide of nitrogen at different temperatures by the methods under consideration, it was requisite to settle certain points relating to the reactions of the body.

In a preliminary determination of specific gravity, made by Dumas' method, some months before the chief investigation, it was found that peroxide of nitrogen was completely absorbed by water, without any evolution of NO_2, at any rate at ordinary temperatures. In that experiment, the Dumas flask filled completely with water when opened under water at the end of the determination; and after several days even, no appreciable amount of gas had made its appearance in the flask.

At first we employed air as the diluent gas in these vapour-density determinations, but were subsequently compelled to have recourse to nitrogen: for direct experiment showed that, when a measured volume of air is sealed up with water and peroxide of nitrogen, absorption of oxygen takes place, the ultimate volume measuring much less than the initial volume of air. Notwithstanding this source of error, which would tend to make the peroxide of nitrogen seem lighter than it really was, the specific gravity of that body at 8·5° C. was obtained as high as 2·46.

The following determinations of the vapour-density of peroxide of nitrogen were made, using as the diluent nitrogen gas, prepared by burning phosphorus in air collected in a gas-holder, finally passing through a strong solution of pyrogallate of potash, and dried with sulphuric acid:—

I.

Vapour-density determination at 97·5° *C.*

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N + NO_4$	263·97	weighing	·4473
„ N .	159·47	„	·2063
	104·50		·2410

Therefore 104·50 c. c. of NO_4 weigh ·2410 grm. Vapour-density = 1·783. Dilute solution of potash (sp. gr. 1·0043) was used to absorb the peroxide of nitrogen. The residual nitrogen was then calculated as being quite saturated with moisture: for potash of so low a specific gravity would not sensibly differ from pure water in point of tension.

In this and the following experiments, it was carefully ascertained that the residual nitrogen was quite colourless: also, on making repeated experiments, no coloration could ever be seen on admitting air to the residual gas.

II.

Vapour-density determination at 24·5° *C.*

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N+NO_4$	425·29	weighing	·8963
„ N .	244·39	„	·3070
	180·90		·5893

Therefore 180·90 C. C. of NO_4 weigh ·5893 grm. Vapour-density = 2·52.

The absorption of NO_4 was made by means of water.

III.

Vapour-density determination at 11·3° *C.*

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N+NO_4$	442·05	weighing	·7556
„ N .	349·4	„	·4390
	92·65		·3166

Therefore 92·65 cub. cent. of NO_4 weigh ·3166 grm. Vapour-density = 2·645. In this determination, strong caustic soda (sp. gr. 1·348) was used to absorb the NO_4. In making the calculation, the gas in contact with such a solution was considered half dry. By this means, absolute precision is sacrificed to certainty. It cannot be doubted that the strong alkali would completely absorb all NO_4 without evolving NO_2.

The influence of the possible tension of aqueous vapour from strong solution of caustic soda does not seriously affect the calculation. If we reckon the gas absolutely dry, we get vapour-density of NO_4 = 2·69.

If absolutely wet, we have vapour-density of NO_4 = 2·60.

IV.

Vapour-density at 4·2° C.

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N+NO_4$	354·38	weighing	·5711
„ N .	294·15	„	·3695
	60·23		·2016

Therefore 60·23 C. C. of NO_4 weigh ·2016 grm. Vapour-density = 2·588.

Here weak solution of caustic potash (sp. gr. = 1.0045) was employed, and considered to have the same tension as pure water.

The results obtained were as follows:—

Temperature.	Vapour-densities.
At 97·5° C	1·783
„ 24·5°	2·520
„ 11·3°	2·645
„ 4·2°	2·588

The vapour-density of NO_4, given in Regnault's "Cours Elémentaire de Chimie;" is 1·72,—a number which is a little less than the first number in the preceding list:—

The formula NO_4 requires $\frac{46}{2} \times {\cdot}0691 = 1{\cdot}5893$.

The formula N_2O_8 requires $\frac{92}{2} \times {\cdot}0691 = 3{\cdot}1786$.

It will be observed that, even at 97·5° C., the vapour-density of peroxide of nitrogen is rather too high for the first formula, whilst at 24·5° and downwards, the vapour density is much nearer that required by the second formula than that required by the first.

If it be allowed that there exist two peroxides of nitrogen, NO_4 and N_2O_8, and that these bodies pass readily into one another, the above results find a simple and natural explanation. At 100° C., the gas consists chiefly of NO_4; at ordinary temperatures, chiefly of N_2O_8; whilst at intermediate temperatures, intermediate quantities of NO_4 and N_2O_8 are present.

If change of composition be denied, the peroxide of nitrogen must have an expansion-coefficient widely differing from that of other gases. To admit such an exception to one of the best physical generalisations, seems unphilosophical.

In general, gases when exposed to pressures not exceeding the usual barometric pressure, and when no incipient liquefaction is taking place, have an expansion-coefficient not differing widely from ·00366. No exception has yet been established; for, in those cases of which sulphur is the representative, it is at least probable that truly polymeric bodies exist.

Another illustration of the vapour-density methods above described consists in an inquiry into the existence of hydrated oxide of ammonium.

Can hydrated oxide of ammonium exist at 100° C., and in the gaseous state? To solve the problem, a quantity of dry ammonia was measured over mercury, then a small portion of water, which had been accurately weighed in a thin glass bulb, was introduced into the ammonia. The whole was then heated up to 100° C., and the volume of mixed gas and aqueous vapour noted. It will be obvious that the formation of hydrated oxide of ammonium would be indicated by contraction. If, on the other hand, the NH_3 and aqueous vapour, when mixed, had the same volume as when separate, no hydrated oxide of ammonium had been produced.

The following are the details of the experiment:—

	Observed volume in Cub. Centimeters.	Temperature Centigrade.	Pressure in Millimeters.	Corrected Vol. in Cubic Cent. at 0° C. and 760 m. m.
Vol. of dry NH_3, ...	34·19	12·5°	558·08	24·008
Vol. of NH_3 + water, ..	107·32	102°C.	709·66	72.973

·0402 grm. of water taken.

But ·0402 grm. of water, when converted into vapour, measures 49·95 cub. centimeters at 0° C. and 760 mm. The difference between the readings before and after the addition of that amount of water is 48·965 cub. cent. Therefore, at 100° C., ammonia and aqueous vapour can exist side by side without suffering any considerable contraction.

XXIX.—*On the Production of a Blue Substance by the Electrolysis of Sulphate of Aniline.*

By H. Letheby, M.B., M.A., Ph.D., &c.

[Professor of Chemistry in the College of the London Hospital.]

Having had to investigate two cases of fatal poisoning by nitrobenzol, and finding that this compound is changed in the living stomach into aniline, I was led to enquire into the chemical reactions of this alkali, in the hope of discovering a delicate and certain test for it. That which first commanded my attention was the fact, that a salt of aniline, under the influence of nascent oxygen, from any source, acquired a blue or purple colour. But the reactions were not in all cases equally delicate, a $\frac{1}{1000}$ of a grain of aniline in half a drop of dilute sulphuric acid (1 to 1) gradually became blue when treated with a little peroxide of lead, or red prussiate of potash, but it required about double this quantity of aniline to show the blue or purple reaction with peroxide of manganese or bichromate of potash; and it was hardly possible to bring out the distinctive colours with less than the $\frac{1}{100}$ part of a grain, with peroxide of hydrogen, peroxide of barium, chlorine or chloride of lime. Referring to my original experiments with strychnine, in which I found that a sulphatic solution of the alkaloid was instantly coloured deep blue, when placed upon a strip of platinum and brought under the influence of the nascent oxygen from the positive pole of a galvanic battery, it occurred to me that the same mode of manipulation with aniline would be attended with a like result. I therefore took a little of the alkali and dissolved it in dilute sulphuric acid (about 1 to 1), and placed a single drop of the solution on a strip of platinum; the platinum was brought into contact with the positive pole of a small Grove's battery (3 inches by 2), and the solution was touched with the negative pole. Instantly the liquid acquired a purple and finally a pinkish colour. This reaction was distinct and very fully characteristic when only the $\frac{1}{2000}$ of a grain of aniline was used. It was, therefore, by far the most delicate of all the nascent oxygen tests for the alkali.

In the course of my medico-legal enquiries, however, I found that, with strong solutions of the alkali, the colour was not violet but deep blue, and sometimes greenish blue, and that the pigment adhered as a fine powder to the platinum. It occurred to me, therefore, that it would be interesting to procure this pigment in a somewhat large quantity in order that its nature might be ascertained. About two ounces of aniline were dissolved in dilute sulphuric acid, and placed in a large beaker. It was then brought under the electrolytic action of two sets of Grove's batteries (each 6 inches by 4) arranged for intensity. A sheet of platinum 6 inches by 4 was placed in the aniline solution and brought into contact with the positive pole of the battery, a flat porous cell containing dilute sulphuric acid was also placed in the solution, and this was connected by a similar sheet of platinum with the negative pole of the battery. By this arrangement, the nascent hydrogen from the negative pole was kept apart from the aniline solution, so that the nascent oxygen from the positive pole might have free and undisturbed action on the aniline. Very soon the positive sheet of platinum became covered with a thick layer of dirty bluish-green pigment. This was removed, and, after being well washed with water, was collected in a filter and dried. Its leading properties are as follows :—

It occurs in the form of a dirty bluish-black powder, which is insoluble in water, alcohol, ether, ammonia, &c. While it rests on the platinum, it acquires a brilliant blue colour by immersion in ammonia, but the blue pigment does not dissolve.

Concentrated sulphuric acid dissolves it, and forms a blue, a green, or a violet solution according to the degree of concentration; and when the solution is diluted with water, a dirty emerald green powder subsides. This is also made blue by concentrated ammonia, and blue or purple by concentrated sulphuric acid.

The blue pigment is partly decolorized by reducing agents, or lime and sulphate of iron; and in this condition it dissolves, and, like indigo, acquires a blue colour on exposure to the air.

The dry pigment is decomposed at a red heat, evolving water and sulphurous acid, and leaving a black cinder.

The composition and chemical reactions of the pigment are now being investigated by Mr. Fewtrell and myself, and will be hereafter the subject of communication to the Society. The present note is merely intended as an exposition of the fact, that a blue pigment is produced by the electrolytic oxidation of a sulphatic solution of aniline.

XXX.—*On the Properties of Liquid Carbonic Acid.*

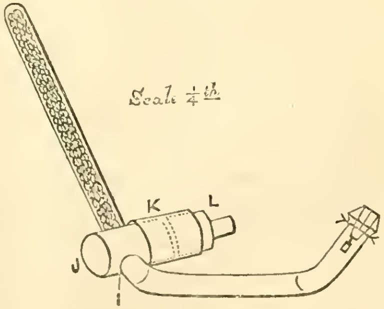
By George Gore, Esq.

[Abstracted from the Philosopical Transactions, 1861, Part i.]

1. A stout glass tube, of the form shewn in Fig. 1, was filled in its distant limb with small pieces of sesqui-carbonate of ammonia, the last pieces of which were pushed in firmly by means of a rod of gutta-percha; the horizontal part was then filled with strong sulphuric acid. A small cup of glass, containing the substance to be submitted to the action of the carbonic acid, was fixed by heat upon the inner end of the gutta-percha stopper; the stopper wetted with a saturated solution of paraffin in chloroform, then forced strongly (with caution) into the mouth of the tube, and secured firmly by transvere binding wire.

2. For convenience of manipulation, the tube was placed in the hole of a transversely perforated cork; the cork fitted rather loosely in a short piece of brass tube; the tube fixed upon a wooden peg, as shown in figure 1, in which I is the hole, J the Cork, K the brass tube, and L the wooden peg with a prolongation of smaller diameter. The cork could thus be readily turned upon its axis, and the glass tube placed and retained in various positions.

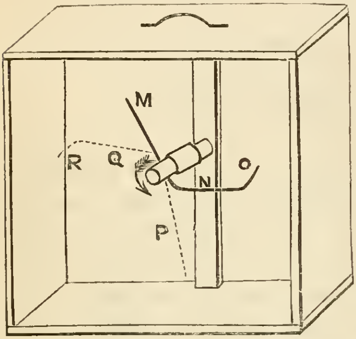
Fig. 1.



3. As a protection from accidents by explosion, and for further convenience of manipulation, a moveable cage or box was con-

structed for each tube; its sides. top, and bottom were made of wood, and its front and back were of fine iron wire-gauze; its dimensions were 12 inches high, 12 inches wide, and 5 inches from front to back; the pieces of gauze were nailed to the wood on one of their vertical edges only, so that they served the purpose of doors. A small vertical strip or piece of wood was fixed at the back part of the box, with a hole at its middle part to receive tightly the small projecting part of the horizontal L, fig. 4. An inspection of fig. 2 will make more clear the whole arrangement.

Fig. 2.



4. The tube, charged with its acid and carbonate, is placed in the frame in the position shown by the lines M, N, O in fig. 2; and the operator having previously protected his hands by thick leather gloves, his eyes by a pair of spectacles, and keeping the wire-gauze door between his face and the tube, occasionally turns the supporting cork upon its axis in the direction of the arrow, so as to cause a little of the acid to flow upon the alkaline carbonate; this must be done with cautious watching and in very small quantities at the commencement, otherwise the bubbles of gas which ascend through the oil of vitriol will carry some of the latter acid into contact with the contents of the little glass cup. The process requires much watching, and if at any time the chemical action is allowed to progress too rapidly, the generating tube is liable to burst in consequence of the heat evolved.

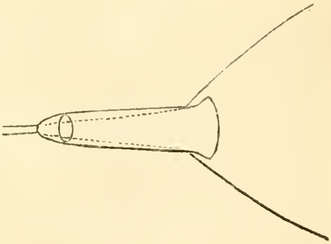
5. The tube is thus occasionally turned until, after the lapse of several hours, it has acquired the permanent position indicated by the dotted lines P, Q, R in fig. 2, when a piece of cotton-wool should be placed upon the stoppered end and saturated with ether, so as to distil off the liberated carbonic acid, and the application of ether be repeated at intervals until nearly the whole of the carbonate is decomposed and the stoppered end of the tube is full of liquid carbonic acid. If the experiment has succeeded well, a length of the tube, equal to 1 or $1\frac{1}{4}$ inch, will, in cold weather, be filled with the liquid acid. By occasionally (once a day or less) applying the ether to the stoppered end of the tube, that part may

be kept full, or partly full, of liquid acid for a long time; I have kept it in this manner during many months.

6. The most frequent cause of failure is the clogging of the tube with sulphate of ammonia; it is rarely that a leakage occurs at the stopper; and the most frequent causes of explosion are, too rapid generation of the gas, and increased temperature of the atmosphere. It is highly advisable never to examine a charged tube without the wire-gauze intervening to intercept fragments of glass, and to use a large moveable screen of glass to protect the eyes from projected oil of vitriol. Nearly all the explosions which occur take place during the process of generating carbonic acid, or within a few days afterwards. The proportion of tubes fractured or burst at different stages of the process is about one-third.

7. In some experiments, where electric sparks were passed through the liquid acid, two longitudinal cuts $\frac{1}{16}$th of an inch deep, were made by a knife on opposite sides of the gutta-percha plug, extending from its smaller nearly to its larger end, before inserting it in the tube; and two fine platinum wires inserted into the cuts and secured very carefully by means of a heated penknife; the inner end of the plug was then coated with melted paraffin, the plug wetted with paraffin solution, and inserted in the usual manner. The wires extended nearly $\frac{1}{2}$ an inch within the tube, and were imbedded for about $\frac{1}{4}$ of an inch, next to the plug in paraffin, the remaining part served for the electrodes. (See fig. 3.) After inserting the plug and securing it by the binding wires, the whole of the outer end of the plug was freely coated with melted paraffin, to insulate more perfectly the electrodes from each other.

Fig. 3.



8. In a first experiment, the electrodes being $\frac{1}{10}$th of an inch apart, and the liquid acid below 32° Fahr., not the slightest conduction occurred with 40 Smee's batteries; and sparks from a Ruhmkorff's coil which passed through $\frac{3}{8}$ths of an inch of cold air would not pass through the liquid acid. And in a second experiment, with electrodes about $\frac{1}{70}$th of an inch apart, sparks from the coil, which were passing freely through $\frac{9}{32}$nds of an inch of cold air, occasionally passed through the cold liquid acid and exhibited a pale blue colour.

9. These experiments show that liquid carbonic acid is a strong insulator of electricity, and that when prepared with concentrated oil of vitriol, and with the precautions stated, it is free from water, sulphuric acid, and sulphate of ammonia. As further proofs of the freedom of the liquid acid from oil of vitriol and water, it may be mentioned,—1st, that dry extract of litmus exhibited no signs of redness by immersion in the liquid acid; 2ndly, a small fragment of glacial phosphoric acid did not appear at all liquefied, or lose the sharpness of its edges after being immersed several weeks; and 3rdly, anhydrous sulphate of copper did not become at all blue in the liquid acid.

10. The following are the results obtained with various solid substances immersed in the liquid acid; some were immersed during several months, many during several weeks, and a few only during several days. The temperature of the liquid acid was generally a little below that of the external atmosphere. Wood-charcoal remained undissolved and unaltered. Anhydrous boracic acid in powder slightly dissolved. White phosphorus slightly dissolved. Glacial phosphoric acid, green solid biphosphide of hydrogen, and ordinary yellow sulphur, undissolved and unchanged. (Bisulphide of carbon absorbs *gaseous* carbonic acid.) Sulphide of phosphorus, and selenium, undissolved and unaltered. Iodine, biniodide of phosphorus, and iodide of sulphur, all dissolved in small quantities (iodine the most freely), and formed red or reddish solutions. Anhydrous hydrochloric acid (prepared by first half-filling the limb A of the tube with sesquicarbonate of ammonia, and then filling the remaining half with hydrochlorate of ammonia) did not produce two strata in the condensed liquid, but imparted to the liquid a brownish colour in each of two experiments, probably by acting upon the gutta-percha stopper. Pentachloride of phosphorus dissolved slowly and formed a colourless liquid. Metallic potassium and metallic sodium slowly acquired bulky white coatings of alkali. Phosphide of sodium, fused chloride of sodium, phosphide of calcium, anhydrous chloride of calcium, bright metallic aluminium, crystals of silicium, anhydrous silica, silico-fluoride of potassium, and arsenic acid, all remained undissolved and unaltered. Terbromide of arsenic and terbromide of antimony, each dissolved slightly. Hydrated crystals of monosulphate of iron became dehydrated and fell to pieces as a white powder, and did not dissolve. Anhydrous sulphate of copper remained white and undissolved; the hydrated salt became white.

Protochloride of mercury and nitrate of silver remained undissolved and unaltered.

11. Cyanide of mercury, oxalic acid, benzoic accid, succinic acid, pyrogallic acid, gallic acid, tannic acid, tannic acid and potash, paraffin, and cocostearic acid remained undissolved and unaltered in appearance. Pitch softened and partly dissolved. Napthalin dissolved in small quantity. Gutta percha; the liquid acid dissolved out the dark-brown colouring matter, and left the gutta percha undissolved, and much more white. India rubber remained black externally, but became perfectly white through the whole of its thickness; on removing it from the acid, it suddenly swelled to a large size, and gradually shrank in a few hours to its orginal dimensions, and afterwards, (in a few days) slowly regained its original colour. Common yellow resin dissolved slightly. Gum-copal remained undissolved. Camphor dissolved rapidly and formed a clear colourless liquid. (Spirit of turpentine dissolves more than its own volume of *gaseous* carbonic acid.) Spermaceti, indigo, pyroxylin, and solid extract of litmus remained undissolved and unaltered. Gamboge dissolved in minute quantity and formed a slightly yellow liquid.

12. These experiments show that liquid carbonic acid is a chemically inert body, and is also a very feeble solvent of substances in general, and is not deoxidized by any of the ordinary deoxidizing agents except the alkali-metals

13. The way to discharge the tubes of their contents is to support them over a gutta-percha vessel within the safety-cage, or behind a duble screen of glass and wire gauze, and, protected by gloves, cut off the binding-wires with a pair of nippers; then if the stoppers are not blown out, pour boiling water upon them. Sometimes the explosion occursimmediately upon cutting the wires, but in most cases it requires the application of the hot water; this is a most convincing proof of the tightness of the stoppers, as the pressure of liquid carbonic acid (according to different authorities) varies from 500 to 1,100 pounds per square inch, according to the temperature of the atmosphere. The tubes nearly always break by the violence of the recoil. In many instances a safer plan was adopted; the wires were not cut, but a current of steam was directed upon the stoppers until they were expelled; the discharge was then less sudden, and the tubes were less frequently broken. It would probably be a still further improvement if the lower end of the tube were closed by a stopper in a

similar manner to the upper end; the contents of the tube might then be discharged at that end, and the substances operated upon would then be exposed to less risk of being lost, and of being brought into contact with the acid and saline matters by the discharge.

XXXI.—*On the influence of Atmospheric Pressure upon some of the Phenomena of Combustion.*

By Dr. E. Frankland, F.R.S.

(Abstracted from the Philisophical Transactions for 1861, by the Author.)

In his classical researches upon flame, Davy mentions the influence which compression and rarefaction exert upon combustion in atmospheric air. Speaking of his experiments with compressed air, the performance of which presented considerable difficulties, he says*, "They show sufficiently that (for certain limits at least) as rarefaction does not diminish considerably the heat of flame in atmospherical air, so neither does condensation considerably increase it; a circumstance of great importance in the constitution of our atmosphere, which at all heights or depths at which man can exist, still preserves the same relations to combustion." His attention was also arrested by the light evolved under similar circumstances, although this phase of the subject does not seem to have attracted more than his cursory attention, and he does not appear to have made any exact quantitative determinations of the rate of increase or diminution of the light of combustion. In reference to this point he says†, "Both the heat and light of the flames of the taper, of sulphur, and of hydrogen were increased by acting on them by air condensed four times; but not more than they would have been by an addition of $\frac{1}{5}$ of oxygen." And again‡, "The intensity of the light of flames in the atmosphere is increased by condensation and diminished by rarefaction, apparently in a higher ratio than their heat, more particles capable of emitting light exist in the denser atmospheres, and yet most of these particles in becoming capable of emitting light, absorb heat; which could not be the case in the condensation of a pure supporting medium."

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* Philosophical Transactions for 1817, p. 65.

† Ibid. p. 64.

‡ Ibid. p. 75.

M. Triger, a French Engineer*, records some observations on combustion in compressed air, which were made during some engineering operations of a peculiar kind, carried on in working a bed of coal lying beneath the alluvium on the banks of the river Loire. A stratum of quicksand 59 to 62½ feet thick had to be penetrated; and it was consequently necessary to find some means of excluding the quicksand and water, which it was found impossible to keep out by the ordinary coffer dams. To overcome this difficulty, M. Triger ingeniously employed strong wrought-iron cylinders about 3¼ feet diameter, open below and closed at top. These were gradually sunk in the quicksand, whilst the air inside them was compressed to the necessary extent to exclude the outer semifluid matter. The workmen labouring within these cylinders were exposed to a pressure of about three atmospheres; and it was observed that the candles, by which they were lighted, burnt with much greater rapidity than at ordinary atmospheric pressure. Respecting this rapid combustion M. Triger says, "A la pression de trois atmosphères, cette accélération devient telle que nous avons été obligés de renoncer aux chandelles à mêches de coton pour les remplacer par des chandelles à mêches de fil. Les premiéres brulaient avec une telle rapidité qu'elles duraient à peine un quart d'heure, et elles répandaient en outre une fumée intolerable."

An observant officer of artillery stationed in India, Quartermaster Mitchell, found that the time of burning of the fuses of shells was considerably increased from the diminution of atmospheric pressure at elevated stations. To the results of his experiments I shall presently have to refer in detail.

Finally, J. Le Conte†, in his interesting memoir on the influence of solar light on combustion, expresses the following opinion with reference to the observations of Davy, Triger, and Mitchell: "Thus a variety of well established facts concur in fortifying the conclusions to which we are led by *à priori* reasoning namely, that the process of combustion is retarded by diminution of the density of the air, whilst it is accelerated by its condensation." M. Le Conte did not himself make any experiments on the influence of atmospheric pressure on the rate of combustion.

Such was the state of knowledge and opinion regarding the influence of atmospheric pressure upon the heat and light of combustion, when in the autumn of 1859, whilst accompanying Dr. Tyndal to the summit of Mont Blanc, I undertook some experiments on the effect of atmospheric pressure upon the rate of combustion of candles.

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* Ann. Ch. Phys. [3] iii. 234, 1841.

† Silliman's American Journal of Science and Arts [2] xxiv. 317.

I. INFLUENCE OF ATMOSPHERIC PRESSURE ON THE RATE OF COMBUSTION.

α. *Of Candles.*

In the experiments just alluded to, six stearin candles were first burnt for one hour at Chamonix, the amount of stearin consumed being carefully determined for each candle: the same candles were afterwards burnt for one hour, carefully protected from currents of air, in a tent on the summit of Mont Blanc, the consumption of stearin being again ascertained. The following were the mean numbers obtained:—

At Chamonix . .	9·4 grms. stearin per hour.
Summit of Mont Blanc.	9·2 grms. stearin per hour.

This close approximation of the two results under such widely different atmospheric pressures, goes far to prove that *the rate of combustion of candles is entirely independent of the density of the air*, the slight discrepancy being probably attributable to the difference (21° C.) of atmospheric temperature in the two series of experiments. It is impossible to repeat these determinations in a satisfactory manner with artificially rarefied atmospheres, owing to the heating of the apparatus which surrounds the candle, and the consequent guttering and unequal combustion of the latter. But in an experiment with a sperm candle, which was burnt first in air under a pressure of 28·7 inches of mercury, and then in air at 9 inches pressure, other conditions being as similar as practicable in the two experiments, the consumption of sperm was found to be,—

At pressure of 28·7 inches .	7·85 grms. of sperm per hour.
At pressure of 9·0 inches .	9·10 grms. of sperm per hour.

This experiment, unsatisfactory as it was in several respects, tends to confirm, for higher degrees of rarefaction, the result previously obtained.

β. *Of Time-fuses.*

In a letter dated January 6th, 1855, an extract from which appeared in the "Proceedings of the Royal Society*," Quartermaster Mitchell communicated the results of a series of carefully conducted experiments, proving that the rate of combustion of the fuses of shells was subject to considerable retardation, which he attributed to the diminution of atmospheric pressure at elevated stations, causing a more scanty supply of oxygen. The following is a short statement of the results of these experiments, in which three-inch fuses were burnt under different atmospheric pressures :—

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* Vol. vii. p. 316.

	Height of barometer at 0° C.	Elevation above sea-level.	Time of burning.
	inches.	feet.	seconds.
1. Average of 6 experiments. .	29·61	. . . .	14·25
2 Average of 6 experiments	26·75	3000	15·78
3 Average of 4 experiments. .	23·95	6500	17·10
4 Average of 2 experiments. .	22·98	7300	18·125

Comparing the amount of retardation with the corresponding reduction of pressure, we have the the following results :—

Numbers of experiments between which comparison is made.	Diminution of pressure.	Retardation of combustion.
	inches.	seconds.
1 and 2	2·86	1·53
2 and 3	2·80	1·32
3 and 4	·97	1·025

Although the results, as I shall presently endeavour to show are perfectly compatible with those obtained with candles under similar circumstances, yet the subject seemed to me of sufficient technical importance to warrant a repetition and extension of these experiments in artificially rarefied air. For this purpose a large iron cylinder was connected on the one hand with an air pump, and on the other with a piece of gas-pipe 6 feet long and 4 inches internal diameter, the opposite end of the pipe being furnished with an arrangement by which the end of the fuse to be ignited could be introduced air-tight within the pipe, whilst the closed end of the fuse projected about 2 inches into the external air. The fuses were ignited at a given instant by a voltaic arrangement, consisting of ten cells of Grove's battery, an instantaneous contact maker, and a piece of thin platinum wire which was inserted into the priming of the fuse. In order to ascertain with precision the moment when the deflagration was finished, the lateral hole at the posterior end of the fuse was bored through to the opposite side: a piece of thread was passed vertically through this aperture, and secured above to a convenient support, whilst an iron ball was affixed to its lower extremity at a distance of a few inches above an iron plate, upon which the ball fell when the fire reached the thread, thus indicating the moment when under ordinary circumstances, the fire of the fuse would be communicated to the contents of the shell. The pressure was indicated by a mercurial gauge inserted into the gas pipe.

The experiments were made with 6-inch fuses (for which I was indebted to the kindness of my friend Mr. Abel of the Woolwich Royal Arsenal), in the following manner. The fuse being inserted into the end of the gas-pipe, and the necessary degree of exhaustion in the iron cylinder and pipe having been obtained, the fuse was ignited at a given signal. During the continuance of its deflagration, an assistant worked the air-pump so as to prevent any great rise in pressure, whilst another observed the vacuum gauge at the moment when the iron ball dropped. The mean between the pressure at the commencement of the deflagration, and that at the end, was assumed to be the mean pressure under which the fuse had been burnt: but it is obvious that this assumed mean pressure can only be approximative, although the gauge fell very regularly and gradually during the continuance of the deflagration.

The following average results were obtained:—

Average pressure, in inches of mercury.	Average time of deflagration of 6-inch fuse.	Increase of time of burning over preceding observation.	Reduction of pressure corresponding with increase of time.	Increase of time for each diminution of 1-inch pressure.
	seconds.	seconds.	inches.	seconds.
30·40	30·33			
28·25	32·25	1·92	2·15	·893
25·70	34·75	2·50	2·55	·980
22·45	37·75	3·00	3·25	9·25
19·65	41·50	3·75	2·80	1·339
15·95	45·50	4·00	3·70	1·081

There are here evident indications of the rate of retardation being somewhat greater at low than at comparatively high pressures; but, neglecting these indications, the above numbers give 1·043 second as the average retardation in a six-inch or thirty-seconds fuse for each inch of mercurial pressure removed. This result agrees closely with that obtained by Quartermaster Mitchell, if we except those fuses which he burnt at the greatest altitude, and in reference to which some error must obviously have crept in, either as regards the altitude of the station where the fuses were burnt, or the duration of their combustion. The latter source of error is perhaps rendered less improbable, from the fact that only two experiments were made at the greatest altitude, whilst six were performed at two, and four at the third of the remaining stations. The following table shows Mr. Mitchell's results, uniformly with those in the last table. The fuses which he employed being fifteen-seconds or three-inch ones, I have multiplied their times of combustion by two, in order to bring them into comparison with the six-inch fuses which were used in my experiments:—

Pressure in inches of mercury.	Average time of combustion of 6-inch fuse.	Increase of time of combustion over last observation.	Reduction of pressure corresponding to increase of time.	Increase of time for each diminution of 1-inch pressure.
	seconds.	seconds.	inches.	seconds.
29·61	28·50			
26·75	31·56	3·06	2·86	1·070
23·95	34·20	2·64	2·80	·943
22·98	36·25	2·05	·97	2·113

Here, omitting the last determination as abnormal, we have the average retardation, in the combustion of a six-inch fuze, equal to 1·007 second for each diminution of one-inch mercurial pressure, which coincides almost exactly with the number (1·043) deduced from my own experiments.

The results of both series of observations may therefore be embodied in the following law:—*The increments in time are proportional to the decrements in pressure.*

For all practical purposes the following rule may be adopted:—*Each diminution of one inch of barometrical pressure causes a* *retardation of one second in a six-inch or thirty-second fuse.* Or, *each diminution of atmospheric pressure to the extent of one mercurial inch increases the time of burning by one-thirtieth.*

This retardation in the burning of time-fuses by the reduction of atmospheric pressure, will probably merit the attention of artillery officers. These fuzes have hitherto been carefully prepared so as to burn at Woolwich, a certain number of seconds, and the perfection with which this is attained is highly remarkable; but such time of combustion at the sea-level is no longer maintained when the fuses are used in more elevated localities. The ordinary fluctuations of the barometer in our latitude must render the rate of combustion of these fuses liable to a variation of about ten per cent. Thus a fuse driven to burn 30 seconds when the barometer stands at 31 inches, would burn 33 seconds if the barometer fell to 28 inches. The height to which a shell attains in its flight must exert an appreciable influence upon the burning of its time fuse; to a far greater extent, however, must the time of combustion be affected by the position of the fuse during the flight of a rifled shell: as in these projectiles the fuse always precedes the shell, the time of burning must obviously be very much shorter than when the shell and fuse are at rest. In an ordinary shell which rotates upon a horizontal axis, the alternate compression and rarefaction of the air at the mouth of the fuse, although tending to compensate each other, will still leave a considerable balance of compression, which must cause a marked retardation in the rate of burning.

The apparently opposite conclusions to which we are led as regards the influence of atmospheric pressure upon the *rate* of combustion, by the experiments upon candles on the one hand and upon time-fuses on the other, are by no means irreconcileable; in fact, an examination into the conditions of combustion in the two cases scarcely leaves room for the expectation of any other result.

In the combustion of a candle, the radiant heat from the flame first melts the combustible matter in the capsule at the base of the exposed portion of the wick; the capillary action of the latter then elevates the liquefied wax, tallow, or spermaceti into the upper part of the wick, where it is exposed to a temperature which effects its volatilization and decomposition. It is thus evident that the rate of combustion, or at all events the rate of consumption of the combustible matter of the candle, is entirely dependent upon the capillarity of the wick, provided that the radiant heat from the flame is sufficient to keep up a supply of liquefied combustible matter at the base of the wick, and that the temperature of the flame is high enough to volatilize this matter on its arrival near the apex of the cotton. Now as capillary attraction is not altered by variations of atmospheric pressure, and as the temperature of the flame is, as will be shown below, almost entirely independent of the same influence, a diminution in the consumption of combustible matter could only arise from the amount of radiant heat striking the capsule at the base of the wick being insufficient to keep up a supply of melted combustible matter equal to the capillary demands of the wick. There can scarcely be a doubt that the amount of heat radiated from a given area of the lower surface of the flame is diminished by rarefaction owing to the decreasing luminosity of the flame: nevertheless this diminution is compensated by the increased flame surface, the radiant heat from which strikes the capsule when the flame becomes enlarged by rarefaction. Whether this compensation be complete or not is of little importance, since observation shows that, even at the highest degrees of rarefaction, a sufficient amount of heat reaches the capsule to keep up an abundant supply of liquefied combustible matter.

We have therefore no ground for any *à priori* assumption that the combustion of candles ought to go on at a decreased rate in rarefied air; in fact there is one consideration which might lead to the opposite opinion; it is this,—the rapidity of the consumption of a candle obviously depends upon the amount of liquefied wax, &c., which passes up its wick in a given time: this amount is determined, up to a certain maximum limit, by the rapidity with which it is got rid of at the upper portion of the capillary tubes where it is volatilized by the heat of the flame. Now, as the rapidity of volatilization is known to be increased by a reduction of pressure, it follows that a larger amount of the combustible would be thus removed from the upper portion of the wick in rarefied than in compressed air. Nevertheless this influence of reduced pressure must be very small in the case of bodies possessing such high boiling-points as tallow, wax, &c., and hence its influence upon the rate of combustion in rarefied air cannot be perceived.

Opposed to the above facts and considerations stands the observation of M. Triger, that candles burn much more rapidly in air compressed three times, than in air at the ordinary pressure. This discrepancy, the cause of which can now only be conjectured, may perhaps reside in some of the circumstances, described above, under which the experiments were made. The constant supply of compressed air to a chamber such as that in which the candles were burnt, must have occasioned a comparatively high temperature in the atmosphere of the chamber, necessarily causing the candles to gutter. Further, the very imperfect combustion which a candle undergoes at this high pressure would have a tendency to increase the size of that portion of the wick situated within the flame, and which constitutes the surface from which the evaporation of the combustible proceeds. Both these circumstances would, I conceive, practically tend greatly to shorten the time during which a candle would burn, which was precisely the circumstance that alone attracted M. Triger's attention, no quantitative determinations of the weight of combustible matter *actually consumed* having been made.

In the deflagration of time-fuses, the conditions are obviously very diffierent. Here the combustible matter never comes into contact with atmospheric oxygen until it has left the fuse-case; unlike the candle, the composition contains within itself the oxygen necessary for combustion, and a certain degree of heat only is necessary to bring about chemical combination. If this heat were applied simultaneously to every part of the fuse composition, the whole would burn almost instantaneously. This sometimes approximately occurs, when, by the expansion of the wooden case into which the composition is rammed, a slight space is formed between the case and its contents, thus allowing the deflagration to propagate itself between the case and the composition. Under such circumstances the fuse burns with explosive rapidity; and probably the occasional bursting of shells before, or immediately after leaving the guns, may be due in some cases to this cause. Under normal circumstances, however, the fuse burns only at a disc perpendicular to its axis; and the time occupied in its deflagration necessarily depends upon the rapidity with which each successive layer of composition is heated to the temperature at which chemical combination takes place. This heat, necessary to deflagration, is evidently derived from the products of the combustion of the immediately preceding layer of composition; and the amount of heat thus communicated to the next unburnt layer must depend, in great measure, upon the number of particles of these heated products which come into contact with that layer. Now, as a large proportion of these products are gaseous, it follows that, if the pressure of the surrounding medium be reduced, the number of ignited gaseous particles in contact at any one moment with the still unignited disc of composition will also be diminished. Hence the slower rate of deflagration in rarefied air.

II. INFLUENCE OF ATMOSPHERIC PRESSURE ON THE LIGHT OF COMBUSTION.

a. Influence of Rarefaction.

In burning candles upon the summit of Mont Blanc, I was much struck by the comparatively small amount of light which they emitted. The lower and blue portion of the flame, which, under ordinary circumstances, scarcely rises to within a quarter of an inch of the apex of the wick, now extended to the height of one-eighth of an inch above the cotton, thus greatly reducing the size of the luminous portion of the flame.

On returning to England, I repeated the experiment under circumstances which enabled me to ascertain, by photometrical measurements, the extent of this loss of luminosity in rarefied air. The result proved that a great reduction in illuminating effect ensues when a candle is transferred from air at the ordinary atmospheric pressure to rarefied air. At the same time, remarkable, changes in appearance occur in the flame itself, especially at high degrees of rarefaction. During the diminution of pressure down to half an atmosphere, the chief alteration is the gradual invasion of the upper and luminous portion of the flame, by the lower blue and non-luminous part. As the pressure sinks towards 10 inches of mercury, the retreat of the luminous portion of the the flame towards the apex goes on uninterruptedly, but the shape and colour of the flame also begin to undergo very remarkable alterations; the summit becomes more and more rounded, until at 10 inches pressure the flame assumes nearly the form of an ellipse, whilst the blue portion, which now comprises nearly the whole flame, acquires a peculiar greenish tint. Finally, at 6 inches pressure, the last trace of yellow disappears from the summit of the flame, leaving the latter an almost perfect globe of the peculiar greenish-blue tint above-mentioned. Just before the disappearance of the yellow portion of the flame, there comes into view a splendid halo of pinkish light, forming a shell half-an-inch thick around the blue-green nucleus, and thus greatly enlarging the dimensions of the flame. The colour of this luminous shell closely resembles that first noticed by Gassiot in the stratified electrical discharge passing through a nearly vacuous tube containing a minute trace of nitrogen. The colour thus imparted to the electrical discharge undoubtedly constitutes the most delicate test of the presence of nitrogen. In both cases, I believe the coloured light to be due to incadescent nitrogen. Under a pressure of 4·6 inches of mercury, a small gas-flame burning in a glass chimney, 1¼ inch in diameter nearly fills the latter with the pinkish glow just mentioned, which extends to a height of nearly 3 inches above the true flame, forcibly reminding the observer of the electrical discharge through a nearly vacuous tube. The gas-flame did not manifest any tendency to extinction at this low pressure.

In attempting photometrical determinations with candles, it was found that, owing to the irregularities of combustion already noticed, no satisfactory quantitative experiments could be made in artificially rarefied air. Oil lamps proved also equally unsuitable, owing to the gradual ascent of the base of the flame towards the apex of the wick, by which the size of the flame and the hourly consumption of oil were greatly diminished. Recourse was therefore had to coal gas, which, although liable to certain minor disturbing influences, yet yielded results, during an extensive series of experiments, exhibiting sufficient uniformity to render them worthy of confidence.

The apparatus employed consisted of a governor into which the gas was first led, and whence it issued through a T-piece, one branch of which led to a jet which I will call *the standard flame*, at one extremity of a Bunsen's Photometer, whilst the other communicated with a test-meter supplying a second jet which may be conveniently termed *the experimental flame*, and which was placed at the opposite extremity of the photometer; thus the delivery of gas of uniform pressure, at the two stopcocks regulating the supply to the two flames, was secured. The standard flame was shielded from currents of air by a cylindrical glass shade. The vessel or receiver, in which the experimental flame was made to burn under different atmospheric pressures, consisted of a glass cylinder 12 inches high and 4½ inches in diameter, welted and ground at both ends, which could be closed air-tight by ground cast-iron plates, between which and the ends of the cylinders collars of leather were introduced, so as to distribute more evenly the pressure exerted by the nuts and screws of the three steel rods binding together the upper and lower plates. The experimental flame burnt within a glass chimney contracted at top and cemented with plaster of Paris into a stopcock, which opened a communication for the exit of the products of combustion; a similar stopcock inserted into the under plate, served for the admission of air into the cylinder. The gas-delivery tube for the experimental flame passed air-tight through a stuffing box in the upper cover of the cylinder, and was most carefully united with the exit tube of the meter so as to exclude the admission of any trace of air during the experiments, and especially whilst the gas was being consumed under reduced pressure.

The atmosphere within the glass cylinder could be uniformly maintained at any pressure from that of the atmosphere downwards, by means of an air-pump and a cylindrical reservoir. The latter was constructed of wrought iron, and, having a capacity of 2¾ cubic feet, served to maintain a very constant pressure unaffected by the intermittent action of the air-pump. The pressure in the reservoir, and consequently in the glass cylinder was indicated by a gauge, which was usually worked with mercury, but occasionally, as described below, with water.

Such is a general outline of the arrangement of the apparatus used: but the following additional particulars may serve to illustrate more fully the mode in which the experiments were conducted. The test-meter was constructed in the usual manner so as to show, by observations of one minute's duration, the rate of consumption per hour; but, in order to ensure greater accuracy, these observations were always extended over a space of at least five minutes, and were repeated at intervals during the course of the determinations at each particular pressure. In order to have the rate of admission of gas to the experimental flame perfectly under control, a micrometer stopcock was inserted in the exit-tube of the meter. Just above the internal orifice of the stopcock for the admission, was placed a circular disc, so as to prevent the current of air from impinging upon the experimental flame; by this arrangement, the latter always burnt with perfect steadiness.

It is well known that the illuminating effect of a gas-flame depends very considerably upon the velocity of the current of air in which it burns, and that the maximum illuminating effect is always produced when the velocity of the current of air is only just sufficient to prevent the escape of unconsumed fuliginous matter; in other words, a maximum of light is obtained from a gas-flame, other things, being equal, when that flame is maintained just below the *smoking point*. This condition of maximum luminosity was carefully secured in all the following determinations, by regulating the admission of external air, and thereby the velocity of the current in the chimney, which was always in free communication with the reservoir and air-pump. When, however, the experimental flame was burning at atmospheric pressure, the cock for the admission of air was removed, leaving a large aperture, whilst the current through the chimney was regulated by the cock at the top of the latter. The extremity of the gas-delivery tube was narrowed to a circular aperature 1·5 millimetre in diameter (about $\frac{1}{17}$th inch), thus forming a burner of such magnitude, as not only to prevent the gas from being discharged from the jet with more than the smallest possible pressure, but also to render the difference of pressure between the gas in the delivery-tube and the air in the glass cylinder practically the same in all the observations.

Each series of experiments was made in the following manner:— The standard flame was lighted, and its rate of consumption regulated to about ·6 or ·7 cubic foot per hour. The absolute amount of gas consumed by this flame was obviously not material, provided that its rate of consumption and conditions of combustion did not vary during the continuance of any one series of experiments. This constancy in the rate and conditions of combustion was secured by the governor. The exhaust cock being closed, and the pressure in the glass cylinder reduced to about 6 inches of mercury, the air-inlet cock was removed, the exhaust cock slightly opened, and the experimental flame ignited by the introduction of a small taper through the open aperature from which the air-inlet cock had been removed: the latter cock was then replaced, and gradually turned so as to cut off all but the necessary supply of air, whilst the exhaust cock was at the same time gradually opened so as to equalize the pressure in the glass cylinder and in the reservoir. With this diminution of pressure in the glass cylinder, it was of course necessary simultaneously to reduce the size of the aperture through which the gas passed from the meter to the burner; and this was effected by a micrometer cock attached to the test-meter. The pressure was now allowed to rise until it reached the lowest point at which a series of observations was to be made: at this point it was then maintained constant by the steady working of the air-pump. The consumption of gas in the experimental flame having been now accurately adjusted to ·65 cubic foot per hour, and all extraneous light excluded from the room, a preliminary observation was made of the illuminating power of the experimental flame as compared with the standard. Owing to the gradual heating of the apparatus surrounding the experimental flame, the temperature, and consequently the luminosity of the latter, underwent a gradual and not unimportant increase, which continued for about an hour, when the illuminating power became perfectly constant. As soon as this constancy of light had been obtained, twenty observations of the illuminating power were made. The pressure in the glass cylinder was then suffered to rise to the point at which the next observations were to be made. The consumption of gas was again carefully adjusted to ·65 cubic foot per hour, when twenty photometrical observations were again made. Similar sets of observations at the remaining higher pressures up to the full atmospheric pressure completed the series.

In the following mean tabulated results, the illuminating power of the standard flame is assumed to be 100, whilst the numbers given under the several pressures represent the luminosity of the experimental flame compared with this standard. In all the series of observations, the consumption of gas by the experimental flame was ·65 cubic foot per hour, measured at the atmospheric pressure :—

First Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver =

6·6 in. mercury.	9·6 in. mercury.	14·6 in. mercury.	19·9 in. mercury.	24·9 in. mercury.	29·9 in. mercury.
1·1	6·5	24·2	63·5	90·0	119·97

Second Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver =

10·2 in. mercury	12·2 in. mercury	14·2 in. mercury	16·2 in. mercury	18·2 in. mercury	20·2 in mercury	22·2 in. mercury	24·2 in. mercury	26·2 in. mercury	28·2 in. mercury	30·2 in. mercury
4·3	14·9	23·6	34·9	44·4	56·8	72·9	86·8	95·7	108·6	118·8

In order to bring the two series of observations into more strict comparison with each other, and with following determinations, it will be convenient to reduce the mean experimental numbers to a standard of illuminating power, in which the light at the maximum pressure, that is the full atmospheric pressure, is assumed to be 100. We then get the following numbers:—

First Series.

Pressure of air in receiver in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.
29·9	119·97	100·0
24·9	90·0	75·0
19·9	63·5	52·9
14·6	24·2	20·2
9·6	6·5	5·4
6·6	1·1	·9

Second Series.

Pressure of air in receiver in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.
30·2	118·8	100·0
28·2	108·6	91·4
26·2	95·7	80·6
24·2	86·8	73·0
22·2	72·9	61·4
20·2	56·8	47·8
18·2	44·4	37·4
16·2	34·9	29·4
14·2	23·6	19·8
12·2	14·9	12·5
10·2	4·3	3·6

These numbers show that even the natural oscillations of atmospheric pressure produce a considerable variation in the amount of light emitted by gas-flames; and, as such a variation is of interest from a technical point of view, it appeared to me of sufficient importance to warrant a special series of observations within, or nearly within, the usual fluctuations of the barometrical column. In order to attain greater delicacy in the pressure-readings in these experiments, a water-gauge was substituted for a mercurial one, but its indications are translated into inches of mercury in the following tabulated results :—

Third Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver =

27 2 in. of mercury.	28·2 in. of mercury.	29·2 in. of mercury.	30·2 in. of mercury.
70·3	74·7	79·2	83·4

Reducing the means of these results, as before, to the maximum standard of 100, we have the following numbers :—

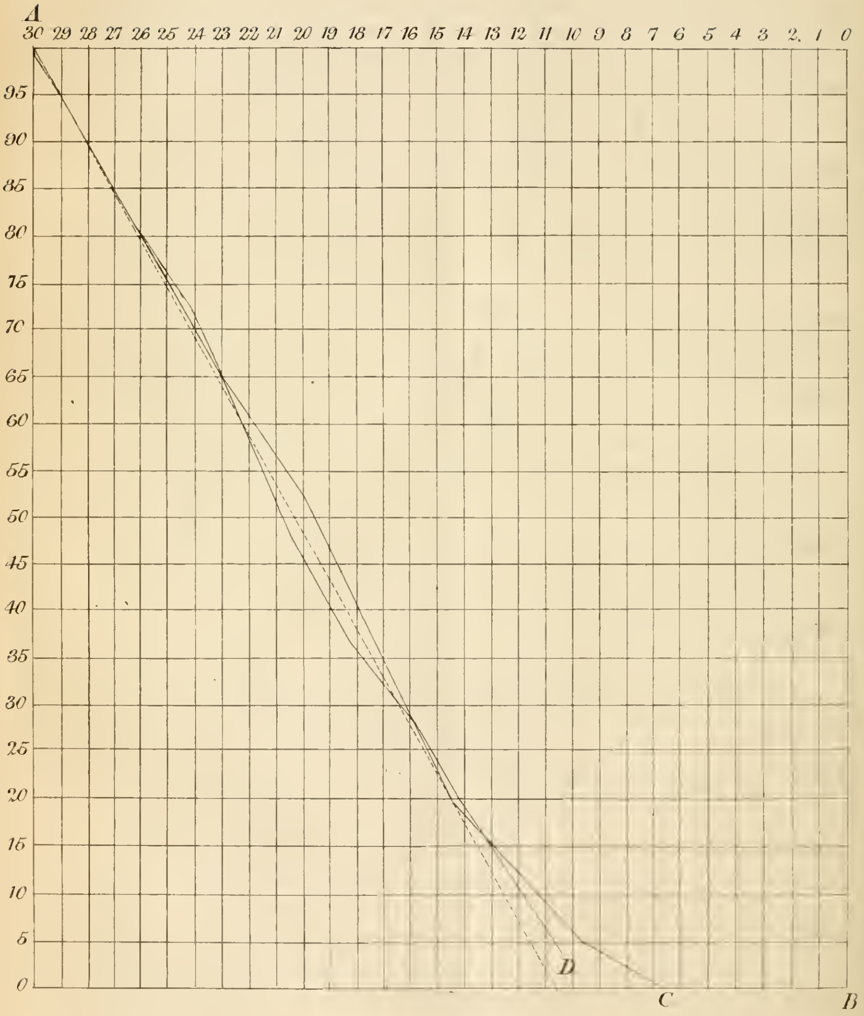
Third Series.

Pressure of air in receiver in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.
30·2	83·4	100·0
29·2	79·2	95·0
28·2	74·7	89·6
27·2	70·3	84·3

It is thus evident that the combustion of an amount of gas which will give a light equal to 100 candles when the barometer stands at 31 inches, will yield light equal only to 84·3 candles when the barometer falls to 28 inches. Such a variation in the luminosity of gas-flames with the oscillations of the barometer will obviously elude the ordinary modes of taking the illuminating power of gas, inasmuch as the standard light with which the gas is compared is also subject to the same influence. Still, although the relative light of gas as compared with candles may remain nearly or quite unaltered, yet its absolute illuminating value depends greatly upon the height of the barometer at the place where it is burnt. Thus a quantity of coal-gas which in London would yield a light equal to 100 candles, would, if burnt in Munich, give an illuminating effect equal to little more than 91 candles; whilst if used to light the city of Mexico, its luminosity would be reduced to 61·5 candles. These numbers are independent of the change of volume by reduced pressure. If equal volumes of the same sample of coal-gas were consumed in London and Mexico, the illuminating effects would be as 100 : 46·2, the temperature being the same in both cases.

An inspection of the above three series of observations, reveals the fact that the rarefaction of air, from atmospheric pressure downwards, produces a uniform diminution of light until the pressure is reduced to about 14 inches of mercury, below which the diminution of illuminating power proceeds at a less rapid rate. This uniformity of relation between pressure and luminosity will be more clearly seen from Diagrams 1 and 2, in which the luminosity is represented by the ordinates, and the pressure by the abscissæ measured from the origin B. If therefore the luminosity were simply proportional to the pressure, the curve of luminosity would coincide with the diagonal drawn from A to B in diagram No. 1. Inasmuch, however, as the diminution of light is more rapid than the diminution of pressure, the lines A C and A D, representing the experimental results of the first and second series of observations, fall between this diagonal and the ordinate corresponding to the point A. Diagram No. 2 shows the results of the third series of observations; in order to render it as open as possible, only that portion of the square is given through which the experimental line A B passes. The line A C in Diagram No. 1, represents the average results of the first series of observations, whilst A D indicates those of the second series. It will be seen, from an inspection of both series, not only that the lines are nearly coincident, but that they do not, down to 14 inches pressure, deviate much from a straight path. This is obviously due to an equal, or nearly equal diminution of light for each equal decrement of pressure down to about 14 inches, below which pressure

Diagram Nº I.


A
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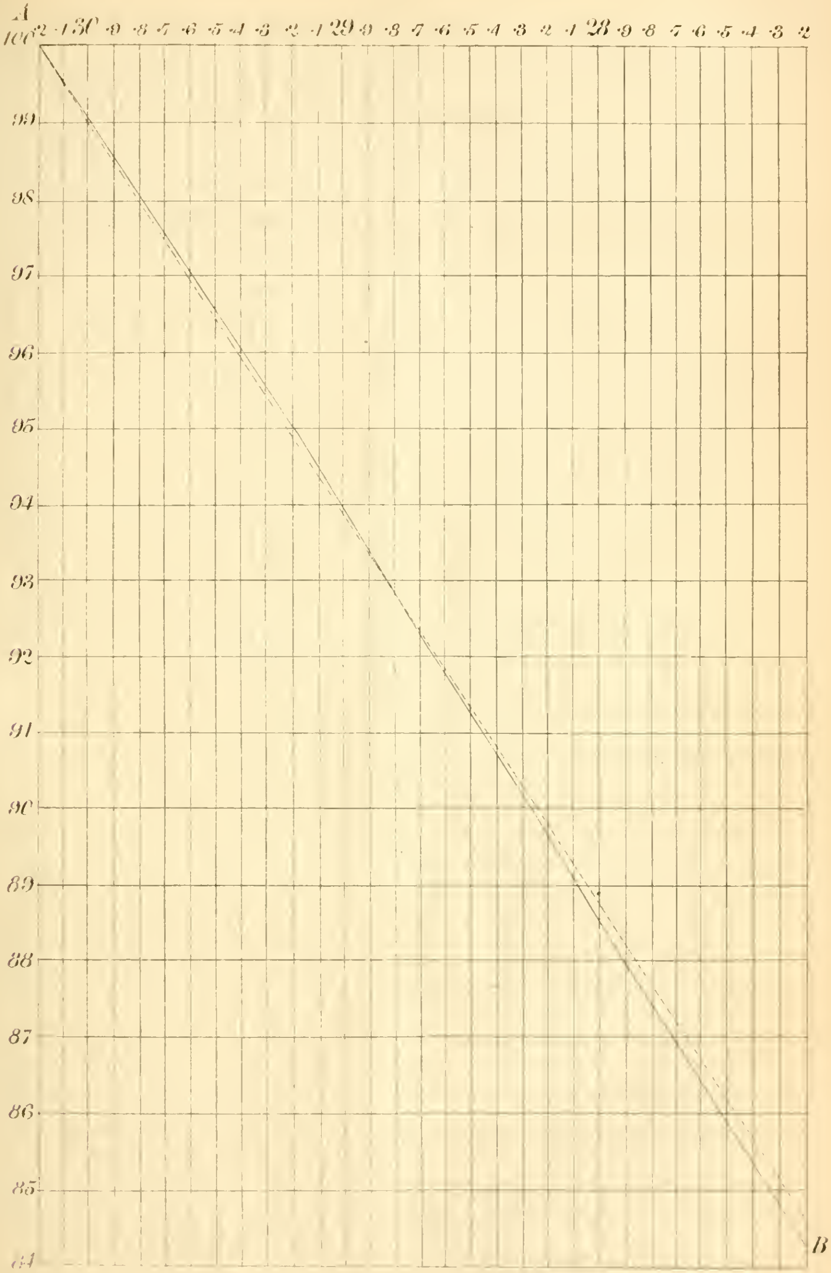
C
B

Diagram No. II.



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both lines deviate markedly from their previous direction, indicating an alteration in the rate of the diminution of luminosity. The mean results of the three series of observations give approximately 5·1 per cent. of the luminosity at 30 inches pressure as the diminution of light corresponding to each diminution of 1 inch of mercurial pressure down to 14 inches. The following Tables exhibit the illuminating effect actually observed, compared with that calculated from this constant:—

First Series.			*Second Series.*			*Third Series.*		
Pressure in inches of mercury.	Illuminating power.		Pressure in inches of mercury.	Illuminating power.		Pressure in inches of mercury.	Illuminating power.	
	Observed	Calculated.		Observed.	Calculated.		Observed.	Calculated.
29·9	100·	100·	30·2	100·	100·	30·2	100·	100·
24·9	75·0	74·5	28·2	91·4	89·8	29·2	95·0	94·9
19·9	52·9	49·0	26·2	80·6	79·6	28·2	89·7	89·8
14·6	20·2	22·0	24·2	73·0	69·4	27·2	84·4	84·7
9·6	5·4	– 3·5	22·2	61·4	59·2			
6·6	·9	–18·8	20·2	47·8	49·0			
			18·2	37·4	38·8			
			16·2	29·4	28·6			
			14·2	19·8	18·4			
			12·2	12·5	8·2			
			10·2	3·6	–2·0			

The dotted lines in Diagrams Nos. 1 and 2 represent the calculated luminosity according to the above Tables. The experimental lines above 14 inches pressure do not, in any part of their course, deviate more from the calculated line than might be expected from the usual errors of experiment. The law of the diminution of the light of gas-flames by reduction of pressure from 30 inches to 14 inches of mercury, may therefore be thus stated. *Of* 100 *units of light emitted by a gas-flame burning in air at a pressure of* 30 *inches of mercury,* 5·1 *units are extinguished by each diminution of one mercurial inch of atmospheric pressure*; or, more generally, *the diminution in illuminating power is directly proportional to the diminution in atmospheric pressure.*

It must, however, here be remarked that the above determinations only establish the constant 5·1 for the particular quality of gas with which the experiments were performed. It still remained to be ascertained whether a flame from gas of a different quality would be amenable to the same rate of reduction; a fourth series of observations was, therefore, made with gas naphthalized to such an extent as nearly to double its illuminating power. The consumption of gas by the experimental flame was, as before, ·65 cubic foot per hour. The following results were obtained:—

Fourth Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver=

6·9 in. of mercury.	9·9 in. of mercury.	14·9 in of mercury.	19·9 in of mercury.	24·9 in. of mercury.	29·9 in. of mercury.
1·00	7·42	28·24	55·54	85·58	114·95

The following Table, calculated from the above, shows that these results are completely in harmony with those obtained with unnaphthalized gas, thus proving that the rate of diminution of luminosity in rarefied air is the same for all hydrocarbon gases, of whatsoever quality, the last two columns being nearly identical down to 14·9 inches pressure:—

Pressure of air in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.	Illuminating power. Calculated.
29·9	114·95	100·	100·
24·9	85·58	74·4	74·5
19·9	55·54	48·3	49·0
14·9	28·24	24·5	23·5
9·9	7·42	6·4	− 2·0
6·9	1·02	·9	−17·3

This series was continued down to 4·6 inches pressure, but the illuminating power of the flame could then no longer be measured by the photometer.

β. *Influence of Compression.*

The foregoing experiments having demonstrated a very remarkable diminution of light in candle and gas-flames by a reduction of atmospheric pressure, it became interesting to ascertain the effect of compressed air upon the luminosity of similar flames. At the very outset of this part of the inquiry, considerable difficulties presented themselves, since it became necessary to abandon a gaseous combustible which could not be compressed to the necessary degree, and then delivered at a uniform pressure through a burner without very complex apparatus. I was thus compelled to resort to solid or liquid combustibles, the irregularities of which were still further increased by the space within the combustion-chamber being necessarily more confined, in order that its walls might the better sustain high pressures. These difficulties in the way of accurate determinations were, however, by no means the most formidable; for it was soon found that any considerable increase of atmospheric pressure caused both candle and oil-flames to throw off large quantities of fuliginous matter, the formation of which could not be prevented by any amount of draught that could be established in the chimney of the apparatus. Hence, although the luminosity of the flames was greatly increased, yet it was obviously much less so than would have been the case under conditions of more perfect combustion. In fact it soon became evident, that the determinations of increase of luminosity by compression must be made in a manner precisely the reverse of that employed for the corresponding determinations in rarefied air; for, whilst in the latter case, the experiments were made with flames, which at ordinary atmospheric pressure were saturated with carbon particles, in the former it was found necessary to commence with flames which were very feebly, or not at all luminous at common pressures. Such is the effect of compressed air in determining the precipitation of carbon particles within the flame, that a small alcohol lamp, which at the ordinary pressure burnt with a pure blue flame, became highly luminous when placed under a pressure of four atmospheres; and it can scarcely be doubted that, at a pressure of five or six atmospheres, its luminosity would be equal to that of sperm oil burning at atmospheric pressure.

The apparatus employed was very similar to that used in the previous part of the inquiry, the gas-delivery tube being replaced by a small lamp, and the comparatively thin and wide cylinder used in the rarefaction experiments by a stronger one, 12 inches long, 2 inches internal diameter, and $\frac{5}{8}$ inch thick. The air was compressed by a forcing pump into a strong reservoir from which it was admitted into the experimental receiver by the air-inlet cock before described, whilst the products of combustion escapes through the exhaust cock which was now made to open into the atmosphere.

The experiments were made in the following manner. The upper cover of the receiver being removed, and the reservoir charged with compressed air, a gentle stream of the latter was turned into the receiver. The lamp was now lighted, and the cover firmly screwed into its place, the exhaust or exit cock being wide open. The admission of air was then regulated so as to produce in the chimney that degree of draught necessary for obtaining the maximum amount of light in the experimental flame. After the latter had been allowed to burn for about half an hour, so as to bring the surrounding glass to a temperature which afterwards remained tolerably uniform, a series of photometrical observations were made. The egress of air through the exit cock was then gradually diminished, whilst the air-inlet cock was fully opened, so as to establish a free communication, and consequently an equality of pressure, between the reservoir and the receiver. The pressure, as indicated by a mercurial gauge was now adjusted, by the more or less rapid working of the pump, to that required for the next series of observations. In practice it was found impossible, with the same liquid in the lamp, to extend any series of observations over a greater range than one atmosphere, owing to the experimental flame beginning to smoke at the higher pressure, if it possessed a measurable illuminating power at the lower one.

Owing to the difficulties above mentioned, I have only been able to obtain satisfactory determinations between one and two atmospheres. In these determinations, the lamp was supplied with amylic alcohol—a liquid which, whilst affording an appreciable amount of light in the experimental flame under one-atmosphere pressure, was found to burn under two atmospheres without smoke, although at a somewhat higher pressure it began to evolve unconsumed carbon. The following mean results were obtained :—

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure in receiver in inches of mercury =

29·7 inches.	59·7 inches.	59·5 inches.
21·2	55·9	55·4

These numbers approximate to those calculated in accordance with the law already given for pressures below that of the atmosphere, thus confirming that law for pressures up to two atmospheres, as is seen from the following comparison, in which the experimental numbers are reduced to the standard of 100 at atmospheric pressure :—

Pressure.	Illuminating power.	
	Observed.	Calculated.
1 Atmosphere	100·	100
2 Atmospheres first ..	263·7	253
2 Atmospheres second ..	261·3	253

Further determinations, in which the illuminating power at three and four atmospheres pressure was compared, yielded results differing widely from this law, and indicating a much more rapid increase of light; but as the liability to errors of observation increases greatly at these higher pressures, I place very little confidence in the numbers obtained, which I will nevertheless here briefly state in the same form as the last Table. In these experiments, the lamp was fed with a mixture of five parts of vinic alcohol and one part of amylic alcohol. The lamp when fed with this mixture had no appreciable illuminating effect under ordinar atmospheric pressure.

Pressure.	Illuminating power.	
	Observed.	Calculated.
3 Atmospheres	406	406
4 Atmospheres	959	559

In endeavouring to trace the causes of this variation of luminosity, it will be convenient first to consider the general conditions upon which the light of flames depends. The luminosity of the flames generally used for artificial light emanates from two sources; viz., first, from the ignition of minute particles of carbon floating in the shell of flame; and secondly, from the incandescence of gaseous matters. The latter source of illumination probably does not usually furnish more than one per cent., of the total amount of light; consequently nearly the whole of the light given out by flames under ordinary circumstances is due, as Davy first pointed out*, to the ignition of solid carbonaceous matter. The light emitted by incandescent gaseous particles becomes, however, much more prominent at very low pressures; and, as this light is not materially influenced by pressure, it causes the deviation from the law of diminution of light, seen at the lower extremities of the lines A C and A D in Diagram No. 1. In order to gain a clear conception of the mechanism of a candle or gas-flame, we must picture to ourselves, first a core of gas or vapour containing hydrocarbons, and secondly a shell of ignited matter closely surrounded on its outside by atmospheric air. The uninterrupted supply of gas or vapour to the core forces the contents of the latter constantly through the ignited shell, at the inner wall of which those hydrocarbons, which cannot exist at a bright red heat, either undergo decomposition into light carburetted hydrogen and free carbon, or imperfect combustion into water, carbonic oxide, and free carbon, or finally perfect combustion into water and carbonic oxide, or even carbonic acid, without any separation of free carbon. The nature of the decomposition or combustion which these hydrocarbons undergo on coming in contact with the ignited shell, thus evidently depends upon the amount of oxygen which gains access to the interior of the shell; if that quantity be insufficient to convert the whole of the carbon of the hydrocarbons into carbonic oxide, the residue will be precipitated, and the flame will be a more or less luminous one; whilst if the amount of oxygen present be sufficient, after burning the hydrogen, to consume the whole of the carbon to carbonic acid, or even to carbonic oxide, no light will be produced from the incandescence of carbon particles.

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* Philosophical Transactions, 1817, p. 64.

Now it is well known that the light of any flame may be increased by increasing the number of carbon particles simultaneously floating in it, provided those particles are consumed before they leave the flame, and are not evolved as smoke. I have also elsewhere shown * that the light of gas-flames, and doubtless that of candles and oil also, greatly depends upon the heat of the flame, the rise in temperature caused by merely heating the air supplied to a gas-lamp, by the waste heat of the flame itself, being sufficient to increase the light to the extent of 67 per cent. without any increased consumption of gas. Such being the conditions necessary for the *increase of light,* it is scarcely necessary to add that the reversal of these conditions, viz., the decrease in the number of particles of carbon existing in the flame at a given time, imperfect combustion allowing the escape of unconsumed carbon, and decrease of temperature in the flame determine a *diminished luminosity*.

One of the first causes which naturally suggests itself to account for the diminution of light by decreased atmospheric pressure, is the diminished amount of oxygen in a given bulk of the supporting medium rendering combustion imperfect, and thus either causing particles of carbon to escape unconsumed, or determining their conversion into carbonic oxide instead of carbonic acid. The effect of the first would be to diminish the luminosity, whilst the second would have the effect of decreasing the light indirectly by diminishing the temperature of the flame. A careful inspection of a gas or candle-flame, burning in an atmosphere undergoing gradual rarefaction, does not afford the slightest evidence of smoke, or even of an increased tendency to throw off fuliginous matter; on the contrary, the tendency to smoke obviously diminishes as the rarefaction progresses; whilst, on the other hand, the fact that an increase of pressure beyond that of the atmosphere causes the most smokeless flames to become smoky, renders utterly untenable the assumption that the escape of unconsumed carbon is one of the causes of diminished luminosity in rarefied atmospheres. Whether or not there is imperfect combustion in the sense of an escape of carbonic oxide instead of carbonic acid from the flame, could not be thus decided, and demanded a closer investigation.

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* Ure's Dictionary of Arts, Manufactures, and Mines, 1860, article "Coal-gas."

To determine this point, I collected samples of the gases escaping from the chimney of the experimental flame (which in this was that of a sperm candle) when burning under atmospheric pressure, and again when burning under a pressure of only 8 inches of mercury. These gases were first treated with caustic potash to absorb carbonic acid; they were then exploded with an equal volume of electrolytic water-gas, and subsequently with excess of hydrogen. The explosion with water-gas caused no contraction, proving the absence of carbonic oxide. The numbers obtained give the following percentage composition of the two samples of gas :—

	Candle burning at atmospheric pressure	Candle burning under 8 inches mercurial pressure.
Nitrogen . .	81·28	81·58
Oxygen . .	11·73	10·30
Carbonic acid .	6·99	8·12
Carbonic oxide .	0·00	0·00
	100·00	100·00

These results prove that in both cases there was no escape of unconsumed combustible gas; consequently *the diminution of light in rarefied atmospheres is not due to imperfect combustion in any form.*

Taken in connexion with the experiments in compressed air, in which imperfect combustion attended with the evolution of fuliginous matter was very marked, these data lead to the remarkable conclusion that *the compression of air renders the* *combustion of gaseous matter less perfect;* and that within certain limits at least, *the more rarefied the atmosphere in which flame burns, the more complete is its combustion.* Thus it is evident, not only that no diminution of light can arise from imperfect combustion in rarefied atmospheres, but also that no reduction of temperature in the flame can occur from the same cause.

A second cause of the diminution of the light of combustion in rarefied atmospheres, and its increase in compressed ones, might be sought for in a possible difference between the temperatures of the flame in the two cases. It is well known that if air be allowed to escape from a vessel into a vacuum, a considerable diminution of temperature ensues in the vessel from which the air escapes; and inasmuch, as the gaseous products of combustion assume a larger volume in rarefied atmospheres than in compressed ones, it can scarcely be doubted that the pyrometric thermal effect of a flame must be diminished to some extent by rarefying the medium in which it burns; nevertheless this effect may be nearly or quite neutralized by the smaller amount of refrigeration caused by the rarefied atmosphere. In order to elucidate this point, a spiral of platinum wire was ignited to visible redness in a flame of hydrogen; on then rarefying the air around the flame and wire, no appreciable alteration in the temperature of the platinum spiral could be noticed. A similar experiment was tried with an alcohol flame, and with the same result. A spiral of platinum wire placed under the receiver of an air-pump, was ignited to visible redness by a voltaic current; on exhausting the receiver, the glow of the platinum gradually increased nearly to whiteness. On readmitting the air, it again diminished to dull redness, showing that the refrigerating effect of rarefied air is much less than that of air at the ordinary pressure. Thus, whilst the temperature produced within a given flame is lowered by rarefaction, the escape of heat from its exterior is hindered by the same process,—the result apparently being that the actual temperature of the flame undergoes but little alteration. This confirms Davy's conclusion, that *rarefaction and compression, within certain limits at least, do not exert any considerable influence upon the heat of flame.*

Although an inquiry into two of the possible causes of the diminution of the light of combustion in rarefied atmospheres has thus failed to afford any explanation of the phenomenon, yet one of them indirectly points to what I believe to be the conditions determinating the variation in illuminating power. If it be true that combustion is more complete in rare atmospheres than in dense ones, it follows that the light of a smokeless flame must decrease with a dimunition of pressure, since, with more perfect combustion, that is, with freer access of oxygen to every part of the flame, there must be a diminution of unconsumed carbon separated within the flame, and consequently a diminished amount of light evolved. In fact, the appearance of the experimental flame during the progress of rarefaction on the one hand, and of compression on the other, can scarcely leave a doubt on the mind of an observer, that the variation of luminosity depends essentially upon the admission of oxygen to that portion of the shell of flame where particles of carbon are usually precipitated, and where consequently the region of luminosity is situated. That an admission of oxygen or air to the interior of a luminous flame has the effect of greatly diminishing or even practically annihilating its luminosity, has been long known and even utilized in the wire-gauze and Bunsen's burners, where heat and not light is the object of the combustion of gas. But, it may be asked, what conditions are there in the combustion of flame in rarefied air that favour the admission of a larger proportion than usual of air to the interior of the flame? In reply, it may be stated that there are two conditions in such combustion, both of which directly tend to produce this result. The first of these conditions, and the one to which I conceive nearly the whole of the effect to be due, is the greater mobility of *rarefied* gaseous bodies, which must produce a more rapid admixture of the flame, gases, and external air than would otherwise take place. The second condition is the gradual, though slow, increase in the volume of the flame as the atmospheric pressure decreases, thus causing the flame to present a gradually increasing surface of contact with the exterior air. This alteration in the volume of flame by diminished pressure is more strikingly seen with a sperm candle than with gas. When such a candle burns under a pressure of two atmospheres, its flame presents the appearance of a sharp spike scarcely one-fourth of an inch in diameter at its lower and broadest part, the apex being lost in the dense smoke which issues from the upper portion of the flame. If the pressure be now diminished, the diameter of the spike markedly increases, especially about its centre, until at one-atmosphere pressure the flame assumes its ordinary appearance. On now rarefying the air, the transverse diameter of the flame goes on increasing until, when the pressure is reduced to about 6 mercurial inches, the flame becomes nearly globular with a diameter of about three-fourths of an inch.

Now, as the amount of combustible matter in the flame was maintained constant in the photometrical experiments detailed above, it follows that the increased external flame surface must so alter the conditions of combustion, as to bring the constant amount of combustible matter into contact with a gradually, increasing quantity of oxygen. That a large amount of air does, even under ordinary circumstances, gain access to the interior of gas and candle-flames, has been proved by the interesting researches upon the gases of these flames recently made by Hilgard,* who found 64 per cent. of nitrogen in the interior of a candle-flame, and by Landolt,† who detected 66 per cent. of nitrogen in the interior of a gas-flame; on no occasion, however, did these experimenters find oxygen in the luminous portion of the flame, although it was found in the blue or non-luminous section. I conceive, therefore, that these consequences of diminished pressure, viz., increased gaseous mobility and augmented volume of flame, are quite competent to explain the variations in luminosity resulting from alterations in the pressure of the supporting medium, and that *these variations in illuminating power depend chiefly, if not entirely, upon the ready access or comparative exclusion of atmospheric oxygen as regards the interior of the flame.*

In conclusion, the influence of atmospheric pressure upon the phenomena of combustion may be thus summed up:

1. The rate of burning of candles and other similar combustibles, whose flames depend upon the volatilization and ignition of combustible matter in contact with atmospheric air, is not perceptibly affected by the pressure of the supporting medium.

2. The rate of burning of self-supporting combustibles, like time-fuses, depends upon the rapidity of fusion of the combustible composition, which rapidity of fusion is diminished by the more rapid removal of the heated gases from the surface of the composition. Hence the rate of burning of combustibles of this class depends upon the pressure of the medium in which they are consumed. In the case of time-fuses, the increments in the time of burning are proportional to the decrements in the pressure of the surrounding medium.

3. The luminosity of ordinary flames depends upon the pressure of the supporting medium; and, between certain limits, the dimi-

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* Ann. Ch. Pharm. xcii. 129.

† Pogg. Ann., cxix. 389.

nution in illuminating power is directly proportional to the diminution in atmospheric pressure.

4. The variation in the illuminating power of flame by alterations in the pressure of the supporting medium depends chiefly, if not entirely, upon the ready access of atmospheric oxygen to, or its comparative exclusion from, the interior of the flame.

5. Down to a certain minimum limit, the more rarefied the atmosphere in which flame burns, the more perfect is its combustion.

XXXII.—*On the action of Carbonate of Ammonium on Magnesian Salts.*

By Edward Divers, M.D.

In all works on chemistry—especially analytical—it is stated, I believe, without exception, that carbonate of ammonium precipitates magnesian salts only very imperfectly, or not at all; and that salts of ammonium, when present in excess, entirely prevent this precipitation.* The object of the present paper is to show the singular incorrectness of this statement—since the precipitation is nearly complete—and to give some particulars of the nature of the reaction and the circumstances favouring it.

If dilute solutions of sulphate of magnesium, chloride of ammonium, and carbonate of ammonium be mixed so as to have excess of ammoniacal salt, especially the carbonate, no immediate effect will follow; but by allowing the mixture to stand, formation of a granular crystalline precipitate will always take place in ten minutes or so, if there is a large excess of carbonate of ammonium, in longer time if the excess be less.

Some of the precipitate, washed on a funnel with a dilute solution of carbonate of ammonium, and afterwards with a little water, yielded after ignition 15·86 p. c. of magnesia as the mean of three experiments (I. = 15·80; II. = 15·93; III. = 15·84).

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* H. Rose, speaking of the precipitation of magnesia by phosphate of sodium from ammoniacal solutions, says that the solution must be rendered alkaline by caustic ammonia, not by carbonate of ammonium, as in the latter case, a certain quantity of ammonia-magnesian carbonate is always precipitated together with the phosphate. (*Traité complet de Chimie Analytique*, Paris, 1861, II, 46.)—Ed.

The double carbonate of magnesium and ammonium

$$Mg(NH_4)_2 CO_3 \cdot 2H_2O,$$

containing 15·87 p. c. magnesia, is therefore indicated.*

The following experiments were made to determine the circumstances favouring the precipitation of this salt:

I. Solutions of sulphate of magnesium containing one-tenth of salt, and of commercial carbonate of ammonium and caustic ammonia, made so as to contain as nearly as possible one-seventh of neutral carbonate, were mixed in various proportions, when it was found that simple carbonate of magnesium precipitated unless there were present 4 eq. of carbonate of ammonium to 1 eq. of sulphate of magnesium. When such a mixture was made, a semi-opaque crystalline deposit began to form after a few minutes, on the walls of the vessel, and rapidly increased. Next day the ammoniacal mother-liquor gave *no immediate precipitate* with phosphate of sodium, although a slight one gradually appeared.

II. One equivalent of sulphate of magnesium, it is evident, requires theoretically two equivalents of carbonate of ammonium for its conversion into double carbonate.

Solutions of sulphate of magnesium and of carbonate of ammonium, of the strength used in (I.), were mixed in the proportion of one equivalent of the former to two of the latter, after first adding to one of them different proportions of chloride of ammonium solution containing one-eighth of salt. In these experiments, it was found that nearly one equivalent of chloride of ammonium to one of sulphate of magnesium was required to prevent the precipitation of any simple carbonate of magnesium. In about a quarter of an hour, precipitation of double carbonate set in, which, compared with that in presence of excess of carbonate of ammonium, formed more slowly, gave a more transparent product, and after standing twenty-four hours, was less complete, phosphate of sodium giving an immediate and decided precipitate with the mother-liquor. When four equivalents of chloride of ammonium were added to one of sulphate of magnesium, the results were the same, and precipitation always occurred in presence of any quantity of ammoniacal salt that could at all come within the accepted meaning of the word "excess."

III. The same mixture was made as in (I.), but in addition to the four equivalents of carbonate, 1 eq. of chloride of ammonium was added. The result was the same as that of (I.), except that the precipitation of the magnesia as double carbonate seemed to be even more complete: for next day phosphate of sodium yielded but a mere trace of precipitate with the mother-liquor.

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* See Gmelin's Handbook III, 244.

IV. The next experiments had for their object the investigation of the effects of quantities of carbonate of ammonium insufficient for the conversion of all the sulphate of magnesium into double carbonate. The carbonate of ammonium was added to a mixture of equivalent proportions of sulphate of magnesium and chloride of ammonium. In these cases, no precipitate appeared till next day or even later, but it did eventually appear, even if only a trace of carbonate was added, so as merely to give a faint ammoniacal odour to the solution, taking the precaution to close the vessel to prevent volatilization of the ammonia.

V. Having mixed the solutions in the proportions of one equivalent of sulphate of magnesium, two of chloride of ammonium, and four of carbonate, portions of the mixture were taken before precipitation had commenced, and diluted until there was in five separate experiments one of magnesia in one, two, three, four, and five-thousand parts respectively. No precipitates formed in any after standing for days. But, at the time of making up these solutions, some of each was mixed with more solution of carbonate of ammonium, so as to be rendered strongly ammoniacal, and in all these precipitation occurred after from 24 hours to 3 or 4 days; and this, not in order of their strength in magnesia, but of their strength in carbonate of ammonium, so that the weakest solution, which now contained less than one five-thousandth of magnesia, was one of the first to precipitate, happening to have been somewhat more freely mixed with carbonate of ammonium than the others.

VI. The solubility of the double salt was tried in the following liquids:—Water, and solutions of chloride, carbonate, and bicarbonate of ammonium.

1. In water.—Guibourt states that the double carbonate of magnesium and ammonium is soluble in this medium. Bucholz, on the other hand, says that it decomposes into a soluble double salt containing excess of carbonate of ammonium and an insoluble salt containing excess of magnesian carbonate.

The statement of Bucholz appears to be a mistake, and that of Guibourt must be considered imperfect: for the action of water is as follows.—If the salt be treated with water on a filter, some of it dissolves and some decomposes into its constituent carbonates, so that the filtrate contains double carbonate of magnesium and ammonium together with free carbonate of ammonium, while that which remains on the filter (after washing until magnesia ceases to appear in the filtrate—an operation soon terminated) is found to be carbonate of magnesium only: for when treated with fixed alkali, it yields no ammonia. But if, to a beaker of water, the finely powdered salt be added in small quantities at a time and stirred, it will dissolve perfectly to a considerable extent. When, however, an excess of the salt is added, it is rapidly attacked by the water, which dissolves out the carbonate of ammonium, leaving the carbonate of magnesium in a compact crystalline mass; and not only does this decomposition take place, but the free carbonate of ammonium thus thrown into the solution seems to induce the decomposition of the double carbonate already dissolved: for precipitation of crystalline carbonate of magnesium soon sets in. (This secondary decomposition may be due to the presence of carbonate of magnesium in the free state, instead of that carbonate of ammonium.) But if, as soon as the water ceases to dissolve more of the salt, it be filtered from the excess, a considerable quantity of clear solution passes through before decomposition commences in the remainder. If then any further quantity of the filtrate be prevented entering into that already obtained, the solution will remain clear for a while, after which it will decompose into the separate carbonates. Dilution with water greatly retards this decomposition.

Some of the filtered solution, as completely saturated as could be without decomposition immediately ensuing, was precipitated with phosphate of sodium. 113·66 grms. were thus found to contain 1·5975 grms. of double salt. One part was therefore dissolved in 71·15 of water. The solution gave an immediate gelatinous precipitate (of magnesia) with ammonia.

Some of the same clear solution was left for twenty-four hours, and the crystalline precipitate which had formed, was collected, washed with a very little water, pressed between folds of bibulous paper, and dried. It gave off no ammonia on treatment with potassa. By ignition, 0·82 grm. left 0·244 grm. of magnesia = 29·76 p.c. The neutral carbonate of magnesium with three of water of crystallization contains 29 p. c. of magnesia.

2. In chloride of ammonium solution. In this the double carbonate dissolves sufficiently to yield an immediate, though slight, precipitate with phosphate of sodium. The solution had an ammoniacal odour (the dry double salt has none). *Carbonate of ammonium caused a precipitate in a few minutes in the solution.*

3. In solution of carbonate of ammonium, the double salt

appears almost insoluble. The filtered solution gave a slight precipitate with phosphate of sodium only after a few minutes.

It would seem that the double carbonate is in some way decomposed to a small extent by solutions of carbonate of ammonium, even the strongest. For when the powdered salt has settled down, there remains suspended for some time a slight milkiness, a result which does not occur with water or chloride of ammonium.

Solutions of bicarbonate of ammonium act just as those of the carbonate.

4. The mother-liquor of a solution which had deposited the double salt and contained an access of carbonate of ammonium and a large excess of chloride and sulphate of ammonium, was found to contain one part of magnesia in about 4660 pts. of solution. Ex. V shows that the precipitation would have been much more complete had there been a *large* excess of carbonate of ammonium. Still the result is worth recording, as furnishing an additional illustration of the insufficiency of ammoniacal salt to prevent precipitation of magnesia by carbonate of ammonium.

From the above experiments it seems to be shown—

1. That, contrary to general statements, carbonate of ammonium *does* precipitate magnesian salts in presence of excess of ammoniacal salts.

2. That the precipitate then formed is the double carbonate of magnesium and ammonium.

3. That this salt is soluble to some extent in water, but very slightly so in solutions of chloride and sulphate of ammonium, almost totally insoluble in that of carbonate of ammonium; and that, within certain wide limits, the double salt is less soluble, according to the strength of the liquid, in salts of ammonium, particularly the carbonate.

Besides the analytical bearings of these results, they are also of interest as furnishing us with a cheap and ready mode of preparing the double carbonate of magnesium and ammonium, which it is believed, will be particularly useful in medicine; it also readily yields a neutral carbonate of magnesium, either by the action of water or by a heat not greater than 100° C. This precipitation of the double carbonate may possibly supply the manufacturer with a mode of separating magnesia from its solutions.

The double carbonate of zinc and ammonium does not seem to be formed by a similar method.

XXXIII.—*On the Composition of the Amorphous Deposit of Urates in Healthy Urine.*

By Henry Bence Jones, M.D., F.R.S., F.C.S.

It has long appeared to me desirable that the composition of the sediment deposited from the urine on cooling should be investigated afresh; very few analyses of this substance have been published, great difference of opinion on its composition still exists, and clearer knowledge on this point might lead to some practical result.

In England, on the authority of Dr. Prout, this granular sediment has been considered as urate of ammonia; many years since I showed that it might be urate of ammonia changed in form by the presence of common salt.*

In Germany, on the authority of Heintz, this sediment has been considered as urate of soda; but though he shows that urate of soda, like urate of ammonia, when deposited from a solution of common salt or chloride of ammonium, has a granular instead of the usual crystalline appearance, and that the amorphous deposit might therefore be modified urate of soda, yet he gives analyses which prove that the ordinary deposit has a much more complex composition. In twenty different examinations, he always found that ammonia was present. Soda was always found, and potassa, lime, and magnesia were recognised. The amount of ash varied from 2·98% to 8·02%. He says the sediment consists of urate of ammonia, urate of soda, urate of lime, and more rarely also of urate of potassa and urate of magnesia.†

Scherer, in *Canstatt's Jahresbericht* for 1849, gives four analyses (though the first and the fourth appear to be the same). He also proves that the granular deposit is a complex mixture, and that the amount of each of the different bases, and the sum of all the bases is very variable.

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* *Med. Chir. Transactions*, 1844.

† *Müller's Archiv. für Anatomie*, 1845, p. 246.

The numbers he obtained were—

Uric acid	82·89	80·02	81·31	82·89
Ammonia	2·23	8·29	7·09	2·23
Potassa	2·04	1·38	2·80	2·04
Soda	0·55	2·05	0·17	0·55
Lime	0·56	0·34	0·26	0·55
Phosphate of lime	0·37	2·72	0·51	
Oxalate of lime	0·33			
Colouring matter and loss	11·03	5·20	7·86	11·74

The deposit from healthy urine was subjected to the following examination :—

Qualitative Determination.—The sediment was allowed to settle. The clear urine was poured off, and the sediment was thrown on a filter and washed with dilute alcohol. When the sediment was well washed, it was dried in a watch-glass at the temperature of the air. If any uric acid crystals were detected by the microscope, the sediment was not used for the analysis. Oxalate of lime crystals were almost always found. After sufficient deposit had been collected,—

1st. A portion was burnt, and left a strong alkaline ash.

2ndly. Another portion was diffused in water and boiled; a considerable portion remained undissolved. The insoluble portion proved to be uric acid. The watery solution, when it cooled, gave an amorphous deposit. This deposit was filtered off and washed; one part was burnt, and left a strongly alkaline ash; another part was dissolved in water, and hydrochloric acid was added, which caused a separation of uric acid.

3rdly. A third portion was also boiled with water, the uric acid was separated by filtration, and the fluid was evaporated to dryness; ammonia was distinctly present in the residue.

Hence it appears that this amorphous sediment is decomposed by boiling with water, depositing uric acid, and contains both fixed and volatile alkali.

Quantitative determinations were made to give the amount of fixed and volatile alkali, and to show whether the amount of uric acid was sufficient, or more than sufficient to form acid urates.

When sufficient substance was collected, it was decomposed by acetic acid. The clear solution was filtered from the uric acid and oxalate of lime. To dissolve the oxalate of lime, the uric acid was treated with hydrochloric acid, dissolved in potassa, precipitated by hydrochloric acid, filtered, washed, dried, and weighed.

The clear acetic solution was mixed with hydrochloric acid, and after twenty-four hours' standing, filtered to separate colouring matter, the liquid was then evaporated to the smallest possible bulk, and precipitated by a solution of chloride of platinum and a mixture of absolute alcohol and ether. After twenty-four hours, the precipitate was filtered off, washed with alcohol and ether, dried and heated to redness; the platinum that remained was treated with dilute hydrochloric acid; and the weight of the platinum was then determined.

The hydrochloric acid solution which was filtered from the platinum was evaporated, and the potassa was precipitated by chloride of platinum, washed with alcohol and ether, dried, and heated to redness; the residue was treated with hydrochloric acid, and the platinum then determined. This gave the amount of potassa, and by deducting this from the amount of platinum previously found, the difference gave the amount of ammonia present. In the substance analysed, no lime could be found.

The liquid filtered off from the first platinum precipitate was evaporated, and the residue burnt at a gentle heat; then it was boiled with hydrochloric acid; and the solution was decomposed by a few drops of sulphuric acid, evaporated to dryness, heated to redness, and weighed. From the amount of sulphate of soda found, the soda was calculated.

The different portions of amorphous deposits used for the first analysis were dried at the temperature of the air.

1st Analysis—

Uric acid . . . . . . = 15·24 grs.
Platinum from the 1st precipitate . = 2·53 grs.
Platinum from the 2nd precipitate . = 1·20 grs.
Hence Potassium . . . = 0·51 grs.
,, Ammonium . . . = 0·22 grs.
The weight of sulphate of soda = 0·56 grs. = 0·18 grs. sodium.

Hence the sediment contained—

Potassium	0·51
Sodium	0·18
Ammonium	0·22
Uric acid	15·24

2nd Analysis—

To avoid any loss of ammonia by drying, the damp deposit was mixed with dilute acetic acid as soon as it had been washed with alcohol.

Uric acid . . . . . = 21·92 grs.
Platinum from the first precipitate . = 7·02 grs.
Platinum from the second precipitate . = 2·28 grs.
Hence Potassium . = 0·91 grs.
,, Ammonium = 0·81 grs.
The weight of sulphate of soda = 1·34 grs. = 0·43 grs. sodium.

Hence the sediment contained—

Potassium	0·91
Sodium	0·43
Ammonium	0·81
Uric acid	21·92

3rd Analysis—

The undried sediment was mixed with hydrochloric acid as soon as it was washed.

Uric acid . . . . . . = 15·56 grs.
Platinum from first precipitate . . = 3·32 grs.
Platinum from second precipitate . . = 2·14 grs.
Hence Potassium . = 0·856 grs.
,, Ammonium = 0·203 grs.
The weight of sulphate of soda = 0·86 grs. = 0·273 grs. sodium.

Hence the sediment contained—

Potassium	0·856
Sodium	0·273
Ammonium	0·203
Uric acid	15·56

or,

	1st analysis.	2nd analysis.	3rd analysis.
Uric acid	94·36	91·06	92·11
Potassium	3·15	3·78	5·06
Ammonium	1·36	3·36	1·61
Sodium	1·11	1·87	1·20

If the amount of uric acid required to combine with the bases to form acid urates is deducted from the total amount of uric acid found in the sediment in Scherer's analyses, and in those made in my laboratory, it appears that much more uric acid is present than is required to form acid urates. Thus, in Scherer's analyses, the average of combined uric acid to free uric acid, is as

1 : 1·1, and in my analyses, combined uric acid is to free as 1 : 1.*

It is very evident from these analyses that mixtures of different amounts of urates and uric acid constitute the amorphous sediments of the urine. That the amorphous sediment often differs in its reactions from any mixture of acid urates, is proved by experiments which were made long ago by Berzelius, and by Lehmann.

In the 9th vol. of the *Lehrbuch*, 1840, p. 418–19, Berzelius says, when speaking of the ordinary deposit: "If, after the urine has become thick, it is filtered, and the sediment is washed on the

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* In Scherer's analyses—

	No. 1.			No. 2.		
Ammonia	2·23	require of uric acid	13·61	8·29	require	50·60
Potassa	2·04	„	6·90	1·38	„	4·66
Soda	0·55	„	2·94	2·05	„	10·96
Lime	0·56	„	3·55	0·34	„	2·15
Combined uric acid			27·00			68·37
Free Uric acid			55·89			11·65
Total uric acid found			82·89			80·02
Hence combined is to free		as 1 :	2·04		as 1 :	0·17

	No. 3.			No. 4.		
Ammonia	7·09	require of uric acid	43·28	2·23	require	13·61
Potassa	2·80	„	9·48	2·04	„	6·90
Soda	0 17	„	0·91	0·85	„	2·94
Lime	0·26	„	1·65	0·55	„	3·49
Combined uric acid			55·32			26·94
Free Uric acid			25·99			55·95
Total uric acid found			81·31			82·89
Hence combined is to free		as 1 :	0·42		as 1 :	2·08

In the analyses made in my Laboratory—

	No. 1.			No. 2.			No. 3.		
Ammonium	0·22	require of uric acid	2·17	0·81	require	8·00	0·273	require	2·01
Potassium	0·51	„	2·16	0·91	„	3·84	0·856	„	3·61
Sodium	0·18	„	1·30	0·43	„	3·12	0·203	„	2 00
Combined uric acid			5·63			14·96			7·62
Free uric acid			9·61			6·96			7·94
Total uric acid found			15·24			21·92			15·56
Hence combined is to free		as 1 :	1·72		as 1 :	0·46		as 1 :	1·04

filter, and water is left to stand on it, often crystals may be found in a few hours."

In the 2nd vol. of his *Lehrbuch*, 1853, p. 355–6, Lehmann says, when speaking of the same sediment when filtered: "If we examine the deposit on the filter directly, or after it has been treated with hot water to dissolve it, endeavour to make it pass through the filter, a quantity of the most beautiful uric acid crystals will be found, whilst in another portion of the same sediment which has not been filtered, not a trace of a crystal can be discovered." "In this experiment, although a large quantity of crystalline uric acid, free from soda, remained on the filter, yet the liquid which passed through the filter had not an alkaline re-action."

Lehmann attributed this liberation of uric acid to a change set up by the colouring matter, and Berzelius considered the crystals as urate of ammonia, formed by the action of the mucus of the urine; but the following experiments will show that the colouring matter and the mucus have nothing to do with the re-action.

On the Decomposition of the Ordinary Amorphous Sediment by washing it with Water.

Experiment 1.—Urine passed at night, gave a deposit in which a few crystals of uric acid were found. It was thrown on a filter, and once washed with water, and then multitudes of crystals of uric acid of a slightly different form were found, mixed with the crystals found before the deposit was filtered.

Experiment 2.—Urine passed at night, gave a deposit containing no uric acid crystals; it was filtered and washed with cold water, and then crystals of uric acid were found.

Experiment 3.—Another deposit contained no crystals. It was filtered, and left two days on the filter unwashed: not a crystal could then be found. It was then washed with water, and crystals immediately appeared.

Experiment 4.—Another uncrystallized deposit was filtered, and examined by the microscope, and not a crystal could be found. It was left 24 hours on the filter unwashed, again examined, and no crystals were found. It was then washed twice with alcohol, and still no crystals could be found even on the following day. It was then washed with cold water, and immediately crystals of uric acid were seen with the microscope.

Experiment 5.—With another deposit this experiment was repeated with the same result precisely.

Experiment 6.—Another deposit was divided into two portions, and both were filtered, the deposit on one filter was washed with urine, and no uric acid crystals could be found; the deposit on the other filter was washed with a solution of common salt, and uric acid crystals were found on the filter.

Experiment 7.—Another deposit, which, when washed with water showed uric acid crystals, was washed with a feebly acid solution of phosphate of soda; no uric acid was found on the filter; but if the sediment was washed with a solution of pure acid phosphate of soda, crystals of uric acid appeared.

In other experiments, the deposit when frequently washed with cold water, gave no uric acid crystals at all. Hot water also frequently dissolved only the urates, and caused the whole deposit to pass rapidly through the filter without leaving any uric acid crystals behind. These deposits gave no uric acid crystals even when boiled with water; the whole deposit dissolved and no crystals could be found. If the sediments showed uric acid crystals when washed with cold water, they also gave the same crystals when boiled with water. Thus, in the qualitative analysis of the amorphous urinary sediment detailed at the beginning of this paper (p. 202), a great portion was found not to be dissolved by boiling water, and this consisted of uric acid crystals.

The following qualitative analyses of the soluble part of the deposit were then made—

4th analysis of the amorphous deposit.

A great quantity of sediment was collected in diluted alcohol; when enough was obtained, it was decomposed by boiling it in water in great excess for five minutes; when quite cold, the clear liquid was drawn off, and the residue was again twice boiled in water. The uric acid which separated was heated with dilute hydrochloric acid to remove any oxalate or phosphate of lime. It was then dried, and weighed 24·30 grs.

The liquid drawn off from the uric acid was mixed with hydrochloric acid, and the uric acid was separated 24 hours afterwards, and dried: it weighed 11·87 grs.

The platinum from the first precipitate containing potassio- and ammonio-chloride of platinum—

= 6·70 grs. platinum.

The platinum from the second precipitate containing potassio-chloride of platinum—

= 3·20 grs.
= 1·27 „ potassium.

Hence the difference 6·70 — 3·23 = 3·50 gives the amount of platinum corresponding to the ammonio-chloride of platinum = 0·63 ammonium.

The weight of the sulphate of soda = 1·13
= 0·36 sodium.

Hence the sediment contained, after boiling with water—

Potassium	1·27 grs.,	requiring to form acid urate	5·41 grs.	uric acid.
Sodium	0·36 grs.	„ „	2·61 „	„
Ammonium	0·63 grs.	„ „	5·84 „	„
			13·86	

Uric acid found 11·87 grs.

5th analysis of the amorphous sediment—

Each separate amount of the sediment as it was collected was boiled with water, and the uric acid that was precipitated was collected.

The uric acid set free by boiling = 16·73 grs.

The fluid drawn off from the uric acid was mixed with hydrochloric acid, and the uric acid separated 24 hours afterwards and dried, weighed 11·37 grs.

The platinum from the first precipitate containing potassio- and ammonio-chloride of platinum = 6·93 grs.

The platinum from the second precipitate containing potassio-chloride of platinum = 2·40 grs.
= 0·95 potassium.

Hence the difference, 6·03 — 2·40 = 3·63 gives the amount of platinum corresponding to the ammonio-chloride of platinum,
= 0·66 ammonium.

The weight of the sulphate of soda—
= 0·93
= 0·30 sodium.

Hence the sediment contained after boiling with water—

Potassium	0·95,	requiring to form acid urate	4·05 grs.	uric acid.
Sodium ..	0·30	„	2·17 „	„
Ammonium	0·66	„	6·12 „	„
Uric acid	11·37		12·34	

From these experiments, it is evident that the amorphous urinary sediments often contain much more uric acid than is required to form acid urates, and that this excess of uric acid is so feebly held in combination by the acid urates, that washing with cold water will set free the crystals of uric acid.

As no combination of this kind was previously known, an attempt was made to form an artificial sediment of urates, which, when washed with cold water or boiled with water, would be decomposed into free uric acid and urates.

On the Artificial Formation of Compounds of the Urates which are decomposed when washed with Water.

Sodium-compound.—Uric acid was dissolved in a heated solution of common phosphate of soda. When the liquid became cold an amorphous precipitate usually was observed. If this was thrown on a filter and washed with water several times, crystals of uric acid appeared.

Impure uric acid from urine was dissolved in a solution of soda, dilute acetic acid was added until the liquid had an acid re-action; on standing, a deposit occurred, which contained no uric acid precipitate; but when it was washed on a filter, uric acid crystals in plenty were observable.

Liebig's artificial urine (formed by dissolving uric acid in a solution of phosphate of soda and adding hippuric acid) was prepared; on standing several hours, an amorphous sediment was deposited, which contained a few crystals of hippuric acid, but the granular matter did not at all resemble the deposit from urine. It was not decomposed by washing with water, but when boiled with water and allowed to cool, a few crystals of uric acid were seen. With different amounts of hippuric acid, different results were obtained. The sediment may be only uric acid, or a sediment decomposable by washing with cold water; or it may be a sediment which cannot be decomposed either by washing or boiling with water.

Pure uric acid was dissolved in soda-ley, and acetic acid was added to the diluted solution until it had a feebly acid re-action; a portion of the precipitate which formed, was thrown on a filter and washed with water, and immediately the previously amorphous sediment was changed into a mass of crystals.

The other portion of the sediment which remained was thrown on a filter and washed with methylated spirit, which produced no effect; no crystals appeared. It was then washed with water, and immediately changed in the same way as before the washing with alcohol.

Potassium-compound.—Uric acid was dissolved in a solution of potassa, and acetic acid was added until the liquid became slightly acid; on standing, an amorphous precipitate fell which was soluble when heated, and contained no trace of free uric acid, but when it was thrown on a filter and washed, sometimes only once or several times with water, crystals of uric acid were found on the filter.

The precipitate was left on the filter for 24 hours before it was washed with water, and no uric acid could be found; it was then washed with alcohol and still no uric acid appeared; but immediately it was washed with water the uric acid was found.

When phosphoric acid was used instead of acetic acid, the same fact was observed.

A portion of the precipitate which had been washed with alcohol, was dissolved in much boiling water. On cooling, crystals of uric acid were separated. The crystals when examined showed no trace of potassa.

Two portions of the amorphous precipitate were taken; one part was washed with fresh urine; this gave no uric acid crystals; the other part was washed with chloride of sodium dissolved in water, and uric acid crystals were found. When a solution of acetate of potassa was used, no crystals of uric acid could be found; nor were any seen when a very feebly acid solution of phosphate of soda was used for washing the amorphous precipitate.

A large quantity of the amorphous potassa sediment, which was decomposable by water, was prepared in order to determine the amount of uric acid and of potassium it contained.

It was well washed with alcohol and then dried in the air. It was then reduced to a fine powder and boiled with much water. The uric acid which deposited by boiling was separated by filtration 24 hours afterwards and weighed.

Weight of uric acid .. .. 11·51 grs.

This uric acid did not contain a trace of potassa.

The liquid filtered from the uric acid was evaporated to a smaller bulk, and filtered 24 hours afterwards, and the small quantity of sediment that fell was rejected. The clear liquid was then evaporated to a much smaller bulk, and on cooling, after 24 hours, a sediment was obtained which was analysed.

The sediment was dried *in vacuo :* 11·43 grs. of substance were taken.

The weight of uric acid was 9·14 grs.

Of sulphate of potassium 4·70 = 2·11 grs. potassium.

9·14 grs. uric acid require to form acid urate of potassium, 2·14 grs. potassium.

	Found.	Calculated.
Uric acid	79·44	80·99
Potassium	18·46	19·01

2nd Analysis.—Another quantity of the sediment which could be decomposed by washing with water, was prepared and boiled as before with water. The uric acid deposited was separated after 24 hours, and dried *in vacuo :* it weighed 6·66 grs.

The fluid which filtered from the uric acid was evaporated to a smaller bulk, and filtered 24 hours afterwards. The weight of the uric acid and urate of potassium on the filter was only 0·16 grs. The clear liquid evaporated to a much smaller bulk, gave a deposit which was filtered after standing 24 hours: it weighed 7·75 grs.; of this, 7·43 grs. were dissolved in water, and hydrochloric acid added as before; the uric acid weighed 5·93 grs.

The liquid filtered from the uric acid was evaporated to dryness, with a few drops of sulphuric acid added.

The sulphate of potassium weighed 2·99 grs. = 1·34 grs. of potassium. 5·93 grs. of uric acid require to form acid urate of potassium 1·39 grs.

	Found.	Calculated.
Uric acid	79·27	80·94
Potassium	18·03	19·01

The decomposable sediment therefore consists of a compound of uric acid with acid urate of potassium.

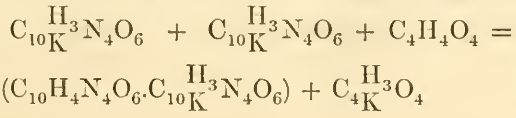
In the 1st experiment :—

The uric acid set free = 11·59 grs., the combined uric acid = 9·14 grs.

In the 2nd experiment :—

The uric acid set free = 6·66 grs., the combined uric acid = 5·93 grs.

Hence when acetic acid acts upon two equivalents of acid urate of potassium, the following equation may represent the result :—



$$C_{10}\substack{H_3\\K}N_4O_6 + C_{10}\substack{H_3\\K}N_4O_6 + C_4H_4O_4 =$$

$$(C_{10}H_4N_4O_6.C_{10}\substack{H_3\\K}N_4O_6) + C_4\substack{H_3\\K}O_4$$

It appears from these experiments, that an artificial granular deposit may be formed, which is decomposed by washing with cold water or by boiling, into uric acid and acid urate of potassium. This granular substance may be considered to resemble the quadroxalate of potassa, which differs from the acid oxalate by containing double the amount of oxalic acid; and following this nomenclature, it may be called *quadrurate of potassa.*

It remains only to show how the statements of Prout and of Heintz have originated.

Dr. Prout discovered the urate of ammonia calculus; this showed that urate of ammonia occasionally, at least, existed in the urine; and in all cases when urates form calculi, it is probable that the urine is so nearly alkaline, that ammonia is apt to be present in the urine; so that by examining calculi containing urates, urate of ammonia would be always likely to occur as the chief constituent.

A number of urinary calculi containing urates were lent me for examination from the museum of St. George's Hospital, and through the kindness of Mr. Stanley, from the museum of St. Bartholomew's Hospital. A portion was scraped from each, and thus enough substance was obtained for an analysis; it was reduced to a fine powder and boiled with water; oxalate and phosphate of lime remained undissolved, but no uric acid. The liquid separated by filtration was mixed with hydrochloric acid, and the uric acid, which separated after 24 hours, was dried; it weighed 13·34 grs. The liquid filtered from the uric acid was evaporated to a small volume, and only a small quantity of uric acid was deposited, which, when dried, weighed 0·93 grs.

The potassa, ammonia and soda were then determined as in the previous analyses. The platinum from the first precipitate containing potassio- and ammonio-chloride of platinum—

= 7·89 grs.

The platinum from the second precipitate containing potassio-chloride of platinum—

= 0·61 grs.
= 0·24 grs. potassium.

Hence the difference 7·89 — 0·61 = 7·28 gives the amount of platinum corresponding to the ammonio-chloride of platinum = 1·32 ammonium.

The weight of the sulphate of soda = 0·49 grs.
= 0·16 grs. sodium.

Hence the calculi contained—

Potasssium	0·24,	requiring to form	acid urate	1·03	uric acid.
Sodium ..	0·16	„	„	1·16	„
Ammonium	1·32	„	„	12·24	„
Uric acid	14·27 = 13.34 + 0·93			14·43	

Hence the calculi consisted chiefly of acid urate of ammonia, and from the analysis of such calculi Dr. Prout probably conjectured that the deposit from the urine consisted of the same substance.

How the statement of Heintz originated it is not very easy to understand; for in his paper from which I have quoted (p. 201), he expressly says that, "the deposit is a mixture of different acid urates modified in form by the presence of other substances in the urine," and he nowhere states that the deposit is urate of soda alone; although he proves by following the experiments which I had made on urate of ammonia (*Med. Chir. Trans.* vol. 27, p. 102, 1844), that needles of urate of soda take a granular form when treated with chloride of sodium or ammonium, or acetate of ammonia.

In conclusion then, it appears that the amorphous deposit of urates in the urine has no constant composition. It is a mixture of different acid urates modified in crystalline form by other substances in the urine. In Scherer's and in my own analyses, the urate of potassium was in larger quantity than the urate of ammonium or the urate of sodium; moreover, uric acid is occasionally found in combination with these acid urates, forming quadrurates, and thus rendering the deposit still more liable to vary in its composition.

Finally, I am much indebted to Dr. Ulrich, for his skill and perseverance in carrying out my wishes in this investigation.

XXXIV.—*Note on Perchloric Ether.*

By Henry Enfield Roscoe.

A body supposed to be perchloric ether, was obtained in the year 1840, by Messrs. Hare and Boyle,* by distilling perchlorate of barium with sulphovinate of the same metal. These observers state that, in explosive violence, this body is not surpassed by any substance known in chemistry, the explosions being produced by heat, friction, or percussion, and often taking place without any apparent cause.

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* Phil. Mag. 37, xix., 370.

I have examined the mode of production of this body, analysed it, and determined its approximate boiling point, and have thereby had frequent opportunity of verifying the statement concerning its extremely explosive nature.

Perchloric ether cannot be obtained by the action of iodide of ethyl upon an alcoholic solution of perchlorate of silver, even at a temperature of — 10° C.; iodide of silver is precipitated, but the perchloric ether yields, with alcohol, perchloric acid and common ether. On bringing perchloric acid $(\mathrm{Cl}\Theta_4\mathrm{H})$ in contact with alcohol or ether, a violent explosion frequently ensues, probably owing to the formation of perchloric ether, but I was unable to prepare any quantity of the ether in this way, even when the mixture was effected at — 20° C. —

Small quantities of perchloric ether may be obtained by distilling perchlorate of potassium with sulphovinate of calcium; but by far the best mode of preparing the substance is that proposed by Hare and Boyle, viz., by distilling the barium-salts of perchloric and sulphovinic acids in nearly equivalent proportions.

An intimate mixture of 10 grms. of crystallized sulphovinate of barium and 10 grms. of perchlorate of barium was, for this purpose, placed in a small retort, the neck of which had been bent downwards; the retort was immersed in an oil bath, and this was slowly heated, a large test-tube containing a small quantity of water, but not otherwise cooled, being used as a receiver. Between 140° and 160°C. tolerably large quantities of a colourless oily liquid heavier than water distilled over; and when the temperature rose to 170°, white fumes of hydrated perchloric acid coming over, the distillation was stopped. About two cubic centimeters of the oil was thus obtained in each operation. After carefully removing the receiver with the distillate, the water, which had a strongly acid re-action, was nearly all drawn off with a pipette, and the oil washed several times with water until the acid re-action was scarcely perceptible. The washed ether was then removed from the superincumbent water by means of a small pipette, care being taken that no water entered the pipette, and the ether immediately brought on to a small dry filter placed upon a wire triangle. After passing through a second filter, the ether dropped into a small glass containing a weighed quantity of alcohol, and as soon as about 20 drops of the ether had fallen into the alcohol, the glass was closed and re-weighed. To the alcoholic solution of the ether, an excess of alcoholic potash was added; this completely decomposed the ether, and after standing for some time, the insoluble perchlorate of potassium was thrown on a weighed filter, washed with alcohol acidified with acetic acid, dried and weighed. The filtrate and wash-alcohol was evaporated to dryness with excess of acetic acid, the residue ignited with peroxide of iron, and the chlorine estimated as silver-salt.

Treated in this way, 0·905 grm. perchloric ether yielded 0·9383 grm. perchlorate of potassium, and 0·0205 grm. chloride of silver.

Hence:—

			Calculated.	Found.
$\cancel{C}_2H_5$	..	29	22·57	....
$\cancel{O}_4$	..	64	49·80	....
Cl	..	35·5	27·63	27·13
		128·5	100·00	

The oxygen, potassium, and chlorine contained in the perchlorate of potassium were severally estimated. Analysis gave the following numbers—

			Calculated.	Found.
Cl	..	35·5	25·63	25·36
$\cancel{O}_4$	..	64·0	46·21	46·65
K	..	39·0	28·16	27·52
		138·5	100·00	99·53

Dry perchloric ether undergoes an explosive decomposition when poured from one vessel to another, or when its particles are in any way slightly shaken. The violence of these explosions is extreme; about 0·2 grm. of the ether contained in a very thin test-tube exploded with such force as to bore a hole 15mm. in diameter and 5mm. deep in a filter-stand of hard wood, and all the glass vessels near were shattered. The greatest care must be taken in working with this body; gloves and glass screens are absolutely necessary. In contact with water, the ether is much more stable, and may then be shaken, or even distilled, without any explosion occurring. Heated under a thin stratum of water, it was found to boil at 74°C. when the barometer stood at 755mm.

XXXV.—*On Liquid Diffusion applied to Analysis.*

By Thomas Graham, F.R.S., Master of the Mint.

[From the Philosophical Transactions, 1862, part i.]

The property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the Diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapour tensions. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol, and sulphate of magnesia. But the substances named belong all, as regards diffusion, to the more "volatile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina, and other metallic peroxides of the aluminous class, when they exist in the soluble form; with starch, dextrin and the gums, caramel, tannin, albumin, gelatin, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to, appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of the class as *colloids,* and to speak of their peculiar form of aggregation as the *colloidal condition of matter.* Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as *crystalloids.* The distinction is no doubt one of intimate molecular constitution.

Although chemically inert in the ordinary sense, colloids possess a compensating activity of their own arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at a high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids, is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a *pectous** modification; and they often pass under the slightest influences from the first into the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid, deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition (H. Rose). The colloidal is, in fact, a dynamical state of matter; the crystalloidal being the statical condition. The colloid possesses ENERGIA. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element), may the characteristic protraction of chemico-organic changes also be referred.

A simple and easily applicable mode of effecting a diffusive separation is to place the mixed substance under a column of water, contained in a cylindrical glass jar of 5 or 6 inches in depth. The mixed solution may be conducted to the bottom of the jar by the use of a fine pipette, without the occurrence of any sensible intermixture. The spontaneous diffusion, which immediately commences, is allowed to go on for a period of several days. It is then interrupted by siphoning off the water from the surface in successive strata, from the top to the bottom of the column. A species of cohobation has been the consequence of unequal diffusion, the most rapidly diffusive substance being isolated more and more as it ascended. The higher the water-column, sufficient time being always given to enable the most diffusive substance to appear at the summit, the more completely does a portion of that substance free itself from such other less diffusive substances as were originally associated with it. A marked effect is produced even where the difference in diffusibility is by no means considerable, such as the separation of chloride of potassium from chloride of sodium, of which the relative diffusibilities are as 1 to 0·841. Supposing a third metal of the potassium group to exist, standing above potassium in diffusibility as potassium stands above sodium, it may be safely predicated that the new metal would admit of being separated from the other two metals by an application of the jar-diffusion above described.

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* Πηκτὸς, *curdled.* As fibrin, casein, albumin. But certain liquid colloid substances are capable of forming a jelly and yet still remain liquefiable by heat and soluble in water. Such is gelatin itself, which is not pectous in the condition of animal jelly; but may be so as it exists in the gelatiniferous tissues.

A certain property of colloid substances comes into play most opportunely in assisting diffusive separations. The jelly of starch, that of animal mucus, of pectin, of the vegetable gelose of Payen, and other solid colloidal hydrates, all of which are, strictly speaking, insoluble in cold water, are themselves permeable when in mass, as water is, by the more highly diffusive class of substances. But such jellies greatly resist the passage of the less diffusive substances, and cut off entirely other colloid substances like themselves that may be in solution. They resemble animal membrane in this respect. A mere film of the jelly has the separating effect. Take for illustration the following simple experiment.

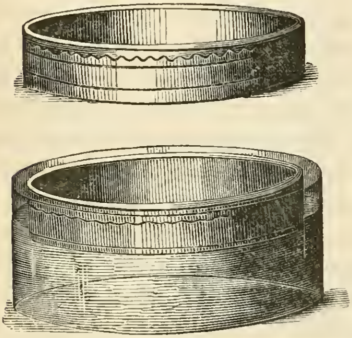
A sheet of very thin and well-sized letter paper, of French manufacture, having no porosity, was first thoroughly wetted and then laid upon the surface of water contained in a small basin of less diameter than the width of the paper, and the latter depressed in the centre so as to form a tray or cavity capable of holding a liquid. The liquid placed upon the paper was a mixed solution of cane-sugar and gum-arabic, containing 5 per cent. of each substance. The pure water below and the mixed solution above were therefore separated only by the thickness of the wet sized paper. After twenty-four hours the upper liquid appeared to have increased sensibly in volume, through the agency of osmose. The water below was found now to contain three-fourths of the whole sugar, in a condition so pure as to crystallize when the liquid was evaporated on a water-bath. Indeed the liquid of the basin was only in the slightest degree disturbed by sub-acetate of lead, showing the absence of all but a trace of gum. Paper of the description used is sized by means of starch. The film of gelatinous starch in the wetted paper has presented no obstacle to the passage of the crystalloid sugar, but has resisted the passage of the colloid gum. I may state at once what I believe to be the mode in which this takes place.

The sized paper has no power to act as a filter. It is mechanically impenetrable, and denies a passage to the mixed fluid as a whole. Molecules only permeate this septum, and not masses. The molecules also are moved by the force of diffusion. But the water of the gelatinous starch is not directly available as a medium for the diffusion of either the sugar or gum, being in a state of true chemical combination, feeble although the union of water with starch may be. The hydrated compound itself is solid, and also insoluble. Sugar, however, with all other crystalloids, can separate water, molecule after molecule, from any hydrated colloid, such as starch. The sugar thus obtains the liquid medium required for diffusion, and makes its way through the gelatinous septum. Gum, on the other hand, possessing as a colloid an affinity for water of the most feeble description, is unable to separate that liquid from the gelatinous starch, and so fails to open the door for its own passage outwards by diffusion.

The separation described is somewhat analogous to that observed in a soap-bubble inflated with a gaseous mixture composed of carbonic acid and hydrogen. Neither gas, as such, can penetrate the water-film. But the carbonic acid, being soluble in water, is condensed and dissolved by the water-film, and so is enabled to pass outwards and reach the atmosphere; while hydrogen, being insoluble in water, or nearly so, is retained behind within the vesicle.

It may perhaps be allowed to me to apply the convenient term *dialysis* to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as *vegetable parchment* or *parchment-paper,* which was first produced by M. Gaine, and is now successfully manufactured by Messrs. De la Rue. This is unsized paper, altered by a short immersion in sulphuric acid, or in chloride of zinc, as proposed by Mr. T. Taylor. Paper so metamorphosed acquires considerable tenacity, as is well known; and when wetted it expands and becomes translucent, evidently admitting of hydration. A slip of 25 inches in length was elongated 1 inch in pure water, and 1·2 inch in water containing one per cent. of carbonate of potash. In the wetted state parchment-paper can easily be applied to a light hoop of wood, or better, to a hoop made of sheet gutta percha, 2 inches in depth and 8 or 10 inches in diameter, so as to form a vessel like a sieve in form (fig. 1). The disc of parchment-paper used should exceed in diameter the hoop to be covered by 3 or 4 inches, so as to rise well round the hoop. It may be bound to the hoop by string, or by an elastic band, but should not be firmly secured. The parchment-paper must not be porous. Its soundness will be ascertained by sponging the upper surface with pure water, and then observing that no wet spots show themselves on the opposite side. Such defects may be remedied by applying liquid albumin, and then coagulating the same by heat. Mr. De la Rue recommends the use of albumin in cementing parchment-paper, which may thus be formed into cells and bags very useful in dialytic experiments. The mixed fluid to be dialysed is poured into the hoop upon the surface of the parchment-paper to a small depth only, such as half an inch. The vessel described (*dialyser*) is then floated in a basin containing a considerable volume of water, in order to induce the egress of the diffusive constituents of the mixture. Half a litre of urine, dialysed for twenty-four hours, gave its crystalloidal constituents to the external water. The latter, evaporated by a water-bath, yielded a white saline mass. From this mass urea was extracted by alcohol in so pure a condition as to appear in crystalline tufts upon the evaporation of the alcohol.

Fig. 1.—Hoop Dialyser.



1. *Jar-diffusion.*

The mode of diffusing more lately followed, which I have already alluded to as jar-diffusion, is extremely simple, and gives results of more precision than could possibly be anticipated. The salt is allowed to rise from below into a cylindrical column of water, and after a fixed time, the proportion of salt which has risen to various heights in the column is observed. The water was contained in a plain cylindrical glass jar, of about 152 millimeters (6 inches) in height and 87 millimeters (3·45 inches) in width. In operating, seven-tenths of a litre of water were first placed in the jar, and then one-tenth of a litre of the liquid to be diffused was carefully conveyed to the bottom of the jar by means of a fine pipette. The whole fluid column then measured 127 millimeters (5 inches) in height. So much as five or six minutes of time were occupied in emptying the pipette at the bottom of the jar, and extremely little disturbance was occasioned in the superincumbent water, as could be distinctly seen when the liquid introduced by the pipette was coloured. The jar was then left undisturbed, to allow diffusion to proceed, the experiments being always conducted in an apartment of constant, or nearly constant temperature. When a certain time had elapsed, the diffusion was interrupted by drawing off the liquid from the top, by means of a small siphon, slowly and deliberately as the liquid had been first introduced, in portions of 50 cubic centimeters, or one-sixteenth of the whole volume. The open end of the short limb of the siphon was kept in contact with the surface of the liquid in the jar, and the portion of liquid drawn off was received in a graduated measure. By evaporating each fraction separately, the quantity of salt which had risen into equal sections of the liquid column was ascertained. From the bottom of two jars, A and B, for instance, a 10 per cent. solution of chloride of sodium was diffused for a period of fourteen days. The whole quantity of salt present in each jar was 10 grammes, which was found at the end to be distributed as follows in the different sectional strata of fluid, numbering them from the top downwards:—

In the first or highest stratum, 0·103 and 0·105 gramme of salt in A and B respectively; in the second stratum, 0·133 and 0·125; in the third stratum, 0·165 and 0·158; in the fourth stratum, 0·204 and 0·193; in the fifth stratum, 0·273 and 0·260; in the sixth stratum, 0·348 and 0·332; in the seventh stratum, 0·440 and 0·418; in the eighth stratum, 0·545 and 0·525; in the ninth stratum, 0·657 and 0·652; in the tenth stratum, 0·786 and 0·747; in the eleventh stratum, 0·887 and 0·875; in the twelfth stratum, 0·994 and 0·984; in the thirteenth stratum, 1·080 and 1·100; in the fourteenth stratum, 1·176 and 1.198; in the fifteenth and sixteenth strata together, 2·209 and 2·324 grammes. With differences so moderate in amount between corresponding strata in the two experiments, this method of observing diffusion may claim a considerable degree of precision.

In similar experiments made at the same time and temperature with sugar, gum-arabic and tannin of nut-galls, the final distribution of each substance was different in each case, and the results may be placed together in illustration of unequal diffusibility, as exhibited by this method of observation. Two experiments were made on each substance, as with chloride of sodium, but the mean result only need be stated.

Table I.—Diffusion of 10 per cent. solutions (10 grammes of substance in 100 cub. cent. of fluid) into pure water, after fourteen days, at 10° (50° Fahr.)

Number of stratum (from above downwards).	Chloride of sodium.	Sugar.	Gum.	Tannin.
1	·104	·005	·003	·003
2	·129	·008	·003	·003
3	·162	·012	·003	·004
4	·198	·016	·004	·003
5	·267	·030	·003	·005
6	·340	·059	·004	·007
7	·429	·102	·006	·017
8	·535	·180	·031	·031
9	·654	·305	·097	·069
10	·766	·495	·215	·145
11	·881	·740	·407	·288
12	·991	1·075	·734	·556
13	1·090	1·435	1·157	1·050
14	1·187	1·758	1·731	1·719
15 and 16	2·266	3·783	5·601	6·097
	9·999	10·003	9·999	9·997

The superimposed column of water being 111 millimeters (4·38 inches) in height, the chloride of sodium, it will be observed, has diffused in sensible quantity to the top, and could have risen higher; the upper layer being found to contain 0·104 gramme of salt, or 1 per cent. of the whole quantity present. The apex of the diffusion-column of sugar appears to have just reached the top of the liquid in the fourteen days of the experiment, for ·005 gramme only of that substance is found in the first stratum, followed by ·008, ·012, ·016, and ·030 in the following strata. Again, no gum appears to be carried by diffusion higher than the seventh stratum (2·2 inches), which stratum contains ·006 gramme, followed by ·031 gramme in the eighth stratum. The minute quantities of substance shown in the first to the sixth stratum, and which do not altogether exceed ·020 gramme, are no doubt the result of accidental dispersion, arising probably from a movement of the upper fluid occasioned by slight inequalities of temperature. The diffusion of tannin is even less advanced than that of gum; but the former numbers are apparently influenced by a partial decomposition, to which tannin is known to be liable, and which gives rise to new and more highly diffusible substances.

Experiments continued, like those last described, for a constant time, do not exhibit the exact relative diffusibilities, although these could be obtained by proceeding to ascertain, by repeated trial, the various times required to bring about a similar distribution and equal amount of diffusion in all the salts. The numbers observed, however, may afford data for the deduction of the relative diffusibilities by calculation.

A particular advantage of the new method is the means which it affords of ascertaining the absolute rate or velocity of diffusion. It becomes possible to state the distance which a salt travels per second in terms of the meter. It is easy to see that such a constant must enter into all the chronic phenomena of physiology, and that it holds a place in vital science not unlike the time of the falling of heavy bodies in the physics of gravitation. It may therefore be not amiss to place here in a short tabular form the results observed of the diffusion of a few more substances, conducted in the same manner as the preceding.

Table II.—Diffusion of 10 per cent. solutions for fourteen days.

Number of stratum (from above downwards).	Sulphate of magnesia, at 10°.	Albumin, at 13° to 13°·5.	Caramel, at 10° to 11°.
1	·007		
2	·011		
3	·018		
4	·027		
5	·049		
6	·085	....	·003
7	·133	....	·005
8	·218	·010	·010
9	·331	·015	·023
10	·499	·047	·033
11	·730	·113	·075
12	1·022	·343	·215
13	1·383	·855	·705
14	1·803	1·892	1·725
15 and 16	3·684	6·725	7·206
	10·000	10·000	10·000

The sulphate of magnesia was anhydrous. The albumin was purified by Wurtz's method. The caramel was partly purified by precipitation by alcohol, as recommended by Frémy, and further by other means which will again be referred to. It will be remarked that the diffusion of sulphate of magnesia exhibited above is very similar to that of sugar in a former Table, but is slightly less advanced. The similarity in diffusibility of these two substances had already been observed in the experiments of former papers. The fall in rate on passing from these crystalloids to the colloids tannin, albumin, and caramel is very striking. The elevation in the liquid column attained by albumin or by caramel is moderate indeed compared with that of crystalline substances. Of albumin, which will be looked upon with most interest, no portion whatever was found in the seven higher strata. It appeared to the extent of 0·010 gramme in the eighth stratum, 0·015 in the ninth stratum, 0·047 in the tenth stratum, 0·113 in the eleventh stratum, 0·343 in the twelfth stratum, while the great mass of this substance remained in the four lower strata. The diffused albumin did not appear to lose its coagulability, or to be otherwise altered. It will be seen immediately that the diffusion of sugar advances as much in two days as the albumin above in fourteen days (Table IV).

The diffusion of caramel is the slowest of all, and does not much exceed in fourteen days the diffusion of sugar in a single day.

It was considered useful to possess examples of the progress of diffusion, in one or two selected substances, for successive periods of time, so as to exemplify the continuous progress of diffusion in these substances. Such a chronological progress of diffusion in a particular substance becomes a standard of comparison for single experiments on the diffusion of other substances. The substances selected were chloride of sodium and cane-sugar.

Table III.—Diffusion of a 10 per cent. solution of Chloride of Sodium in different times.

Number of stratum.	In four days, at 9° to 10°.	In five days, at 11°·75.	In seven days, at 9°.	In fourteen days, at 10°.
1	·004	·004	·013	·104
2	·004	·006	·017	·129
3	·005	·011	·028	·162
4	·011	·020	·051	·198
5	·023	·040	·081	·267
6	·040	·075	·134	·340
7	·080	·134	·211	·429
8	·145	·233	·318	·535
9	·261	·368	·460	·654
10	·436	·589	·640	·766
11	·706	·762	·850	·881
12	1·031	1·090	1·057	·991
13	1·416	1·357	1·317	1·090
14	1·815	1·697	1·527	1·187
15 and 16	4·023	3·613	3·294	2·266
	10·000	9·999	9·998	9·999

TABLE IV.—Diffusion of a 10 per cent. solution of Cane-sugar in different times.

Number of stratum.	In one day, at 10°·75.	In two days, at 10°.	In six days, at 9°.	In seven days, at 9°.	In eight days, at 9°.	In fourteen days, at 10°.
1	....	....	·001	·002	·002	·005
2	....	....	·002	·002	·003	·008
3	....	....	·002	·003	·003	·012
4	....	....	·002	·004	·004	·016
5	....	....	·003	·004	·007	·030
6	....	....	·005	·007	·012	·059
7	....	....	·011	·020	·031	·102
8	·002	·002	·024	·051	·072	·180
9	·002	·008	·071	·121	·154	·305
10	·005	·027	·170	·260	·304	·495
11	·024	·107	·376	·507	·555	·740
12	·133	·344	·727	·897	·858	1·075
13	·597	·930	1·282	1·410	1·365	1·435
14	1·850	1·940	1·930	1·950	1·955	1·758
15 & 16	7·386	6·641	5·392	4·760	4·674	3·783
	9·999	9·999	9·998	9·998	9·999	10·003

The scheme of the diffusion of the chloride of sodium may afford terms of comparison for the metallic salts, acids and other highly diffusible substances, while the scheme of sugar will be found more useful in appreciating the diffusion of organic and other less diffusible substances. In comparing the two Tables together, it appears that a fourteen days' diffusion of sugar is greater in amount than a four days' diffusion of chloride of sodium, but less than a five days' diffusion of the same substance. The diffusion of chloride of sodium appears to be pretty nearly three times greater (or more rapid) than that of sugar.

The following experiments were made upon hydrochloric acid and chloride of sodium at a somewhat lower temperature and for times which are different, but which give a nearly equal diffusion for each substance.

TABLE IV. *bis.*—10 per cent. solutions.

Number of stratum.	Hydrochloric acid, in grammes. Three days at 5°.	Chloride of sodium, in grammes. Seven days at 5°.
1	·003	·003
2	·006	·009
3	·012	·010
4	·022	·026
5	·043	·055
6	·086	·082
7	·162	·165
8	·308	·270
9	·406	·403
10	·595	·595
11	·837	·823
12	1·080	1·085
13	1·163	1·270
14	1·578	1·615
15 and 16	3·699	3·589
	10·000	10·000

The diffusion of hydrochloric acid in three days corresponds closely with the diffusion of chloride of sodium in seven days. The times of equal diffusion for these two substances, at the temperature of the experiment, appear accordingly to be 1 (hydrochloric acid) and 2·33 (chloride of sodium). Hydrochloric acid and the allied hydracids, with other monobasic acids, are the most diffusive substances known. The general results of several series of experiments may be expressed approximately by the following numbers:—

Approximate times of equal diffusion.

Hydrochloric acid	1
Chloride of sodium	2.33
Sugar..........................	7
Sulphate of magnesia	7
Albumen	49
Caramel........................	98

It is curious to observe the effect of changing the liquid atmosphere in which diffusion takes place, which is water in all these experiments, and replacing it by another fluid, namely alcohol. Two substances were diffused in the usual manner, but with this difference, that the substances were dissolved in alcohol, and the solutions placed under a column of the same liquid in the jar. The alcohol was of sp. gr. 0·822 (90 per cent.).

TABLE V.—Diffusion of 10 per cent. solutions of Iodine and Acetate of Potash in Alcohol, in seven days.

Number of stratum.	Iodine at 14°.	Acetate of potash, at 14° to 15°.
1	·028	·055
2	·033	·057
3	·046	·061
4	·038	·063
5	·037	·064
6	·039	·066
7	·081	·070
8	·143	·071
9	·263	·072
10	·417	·095
11	·637	·285
12	·936	·619
13	1·235	1·157
14	1·506	1·907
15 and 16	4·561	5·358
	10·000	10·000

TABLE V. *bis.*—Diffusion in Alcohol of a 10 per cent. solution of Resin for seven days, at 14°·5.

Number in stratum.	Diffusate, in grammes.
1	·017
2	·017
3	·018
4	·017
5	·019
6	·020
7	·022
8	·024
9	·025
10	·080
11	·210
12	·498
13	·992
14	1·700
15 and 16	6·341
	10·000

The experiments were conducted in the absence of light, and there is no reason to believe that the iodine acted chemically upon the alcohol. The diffusion is more advanced in the iodine than in the acetate of potash, but in both is moderate in amount, confirming the early experiments with phials, which appeared to show that the diffusion process was several times slower in alcohol than in water. The small quantities of iodine found in each of the six superior strata are nearly equal, and were no doubt accidentally elevated by the mobility of this fluid, arising from its high dilatability by heat compared with that of water at the same low temperature. The diffusion may be considered then as confined to the nine lower strata, and considerably resembles that of sugar in water for eight days.

The diffusion of acetate of potash is still less advanced than that of iodine, and is probably confined to the six lower strata, the salt found in the higher strata presenting in its distribution the appearance of having been carried there by a movement of the fluid consequent upon heat-dilatation, and not by diffusion. The diffusion of acetate of potash in alcohol observed during seven days approximates to that of sugar in water during six days (Table IV).

I now proceed to observations of the simultaneous diffusion of two substances in the same fluid. The great object of this class of experiments was to separate salts of unequal diffusibility, and to test the application of diffusion as an analytical process. A mixture of two salts being placed at the bottom of the jar, it may be expected that the salts will diffuse pretty much as they do when they are diffused separately; the more diffusive salt travelling most rapidly, and showing itself first and always most largely in the upper strata. The early experiments of diffusion from phials had shown indeed that inequality of diffusion is increased by mixture, and the actual separation is consequently greater than that calculated from the relative diffusibilities of the mixed substances. Chlorides of potassium and sodium diffuse nearly in the proportion of 1 to 0·841, according to the earlier experiments. They may afford, therefore, the means of observing the amount of separation that may be produced by a very moderate difference in diffusibility. A mixture of 5 grammes of each salt in the usual 100. cub. cent. of water was diffused.

Table VI.—Diffusion of a mixture of 5 per cent. of Chloride of Potassium and 5 per cent. of Chloride of Sodium, for seven days, at 12° to 13°.

Number of stratum.	Chloride of potassium.	Chloride of sodium.	Total diffusate.
1	·018	·014	·032
2	·025	·015	·040
3	·044	·014	·058
4	·075	·017	·092
5	·101	·034	·135
6	·141	·063	·204
7	·185	·104	·289
8	·252	·151	·403
9	·330	·212	·542
10	·349	·351	·700
11	·418	·458	·876
12	·511	·559	1·070
13	·552	·684	1·236
14	·615	·772	1·387
15 and 16	1·385	1·551	2·936
	5·001	4·999	10·000

In the upper part of the Table chloride of potassium always appears in excess, but not in so large a proportion in the first three strata as in the fourth. This inequality may be partly owing to mechanical dispersion of the mixed solution, but it is to be referred chiefly, I believe, to errors of analysis from a loss of the chloride of potassium difficult to avoid in the determination of minute proportions of that salt by means of chloride of platinum. Of 92 milligrammes of salt found in the fourth stratum, 75 milligrammes, or 81·5 per cent. are chloride of potassium. The first six strata contain together 561 milligrammes, of which 404 milligrammes, or 72 per cent., that is nearly three-fourths, are chloride of potassium. We have to descend to the tenth stratum before the salts are found in equal proportions. The progression is then inverted, and chloride of sodium comes to preponderate in the lower strata.

It is evident that the preceding experiment might be so conducted as to diffuse away the chloride of potasssium and leave below a mixture containing chloride of sodium in relative excess, to as great an extent as the chloride of potassium is found above, in the last experiment.

Further, the mixture in which chloride of potassium was concentrated in the experiment described, so as to form 72 per cent. of the whole mixture, might be again subjected to diffusion in the same manner. In an experiment upon a mixture of 7·5 grammes of chloride of potassium and 2·5 grammes of chloride of sodium, the six upper strata gave 640 milligrammes of salt, of which 610 milligrammes, or 95·3 per cent., were chloride of potassium. It is obvious that, by repeating this diffusive rectification a sufficient number of times, a portion of the more diffusive salt might be obtained at last in a state of sensible purity.

The preceding example illustrates the separation of unequally diffusive metals or bases; the following example represents, on the other hand, the separation of unequally diffusive acids united with a common base. Chloride of sodium and sulphate of soda diffuse separately in the phial experiments in the proportion of 1 to 0·707.

Table VII.—Diffusion of 5 per cent. of Chloride of Sodium and 5 per cent. of anhydrous Sulphate of Soda, for 7 days, at 10° to 10°·75.

Number of stratum.	Chloride of sodium, in grammes.	Sulphate of soda, in grammes.	Total diffusate, in grammes.
1	·009	....	·009
2	·013	·001	·014
3	·024	·002	·026
4	·038	·003	·041
5	·060	·006	·066
6	·095	·012	·107
7	·141	·029	·170
8	·203	·059	·262
9	·278	·115	·393
10	·360	·205	·565
11	·473	·317	·790
12	·560	·507	1·067
13	·637	·694	1·331
14	·718	·909	1.627
15 and 16	1·390	2·141	3.531
	4·999	5·000	9·999

Here the separation is still more sensible than before with the bases. The six upper strata contain 263 milligrammes of salt, of which 239 milligrammes, that is 90·8 per cent., are chloride of sodium. The salt of the upper eight strata amounts to 695 milligrammes, of which 583 milligrammes, or 83·9 per cent., are chloride of sodium.

How long the diffusion should be continued in a liquid column of limited height, such as in these experiments, so as to produce the greatest separation, is a question of some interest, which can only be answered by experiment. The last diffusion was accordingly repeated, with the difference that it was continued for double the former time.

Table VIII.—Diffusion of 5 per cent. of Chloride of Sodium and 5 per cent. of Sulphate of Soda, for fourteen days, at 10° to 11°.

Number of stratum.	Chloride of sodium, in grammes.	Sulphate of soda, in grammes.	Total diffusate, in grammes.
1	·077	·005	·082
2	·089	·009	·098
3	·105	·014	·119
4	·130	·026	·156
5	·161	·044	·205
6	·199	·072	·271
7	·240	·111	·351
8	·289	·173	·462
9	·337	·241	·578
10	·392	·334	·726
11	·433	·433	·866
12	·487	·539	1·026
13	·525	·646	1·171
14	·555	·745	1·300
15 and 16	·979	1·609	2·588
	4·998	5·001	9·999

The salt contained in the three upper strata amounts to 299 milligrammes, of which 271, or 90·6 per cent. of the whole, are chloride of sodium. The upper five strata yield 660 milligrammes of salt, of which 562 milligrammes, or 85·1 per cent., are chloride of sodium. These proportions are not dissimilar to those deduced from the former Table, and show that little is gained in the way of separation by extending the diffusion period from seven to fourteen days, unless indeed the column of fluid be increased in height at the same time.

It might be worth observing whether the separation of two unequally diffusive metals can be favoured by varying the acid, or form of combination: whether, for instance, the hydrates of potash and soda would not separate to a greater extent than has been observed with the chlorides of potassium and sodium, the separate diffusibilities of the former substances being as 1 to 0·7, while that of the latter are as 1 to 0·841. I have not, however, pursued this branch of the subject.

The separation of the same metals from each other may possibly be favoured in another manner. In the preceding experiments (Table VI) the two metals were in union with the same acid, or rather both were in the state of chloride. But the metals might be used in combination with different acids, and these acids themselves might be of equal or of unequal diffusibility. If of equal diffusibility, such as nitric and hydrochloric acids, no reason appears why the acids should affect the amount of separation. But if the acids are unlike in diffusibility, the case is not so clear. If, for instance, the potassium were in the form of chloride and the sodium of that of sulphate, might not the diffusion of the potassium be promoted by the highly diffusive chlorine with which it is associated, and the diffusion of the soda, on the other hand, be retarded by its association with the slowly diffusive sulphuric acid? Will, in fine, the separation of the metals be greater from a mixture of chloride of potassium and sulphate of soda, or even from sulphate of potash and chloride of sodium, than from the two chlorides, or from the two sulphates? The inquiry, it will be remarked, raises the whole question of the distribution of acid and base in solutions of mixed salts. It will be illustrated by a comparison of the diffusion of chloride of potassium mixed with sulphate of soda, with the diffusion of sulphate of potash mixed with the chloride of sodium, the salts being taken in equivalent proportions.

TABLE IX.—Diffusion of a mixture of 5·12 per cent. of Chloride of Potassium and 4·88 per cent. of Sulphate of Soda (equivalent proportions), for seven days, at 14°.

Number of stratum.	Potassium, in grammes.	Sulphuric acid, in grammes.	Total diffusate of the salts, in grammes.
1	·014	·001	·024
2	·017	·001	·030
3	·024	·002	·045
4	·032	·004	·066
5	·046	·008	·097
6	·064	·016	·149
7	·087	·029	·215
8	·121	·052	·316
9	....	....	·441
10	....	....	·615
11	....	....	·815
12	....	....	1·042
13	....	....	1·290
14	....	....	1·517
15 and 16	....	....	3·346
			10·008

TABLE X.—Diffusion of a mixture of 4·01 per cent. of Chloride of Sodium and 5·99 per cent. of Sulphate of Potash (equivalent proportions), for seven days, at 14°.

Number of stratum.	Potassium, in grammes.	Sulphuric acid, in grammes.	Total diffusate of the salts, in grammes.
1	·014	·001	·023
2	·017	·001	·030
3	·024	·002	·044
4	·032	·004	·065
5	·046	·007	·096
6	·064	·015	·149
7	·086	·029	·219
8	·121	·052	·315
9	....	....	·435
10	....	....	·600
11	....	....	·797
12	....	....	1·025
13	....	....	1·261
14	....	....	1·480
15 and 16	....	....	3·467
			10.016

The weight of the mixed salt was always 10 grammes. The diffusions exhibited in the two Tables are strikingly similar, and indeed may be considered as identical. It thus appears that the diffusion of the metals is not affected by the acid with which they are in combination. The result is quite in harmony with Berthollet's view, that the acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of soda is the same thing as a mixture of sulphate of potash and chloride of sodium, when the mixtures are in a state of solution. With two acids greatly unequal in their affinity for bases, the result might possibly be very different.

2. *Effect of Temperature on Diffusion.*

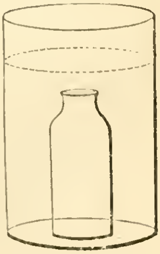
Diffusion is promoted by heat, and separations may accordingly be effected in a shorter time at high than at low temperatures. In a series of observations made upon hydrochloric acid, the diffusion of that substance was carefully determined at 15°·5 (60° F.), and at three higher points, advancing by 11°·11 (20° F.). The ratios of the diffusions observed were as follows:—

Diffusion of hydrochloric acid at 15°·55 (60° F.), 1
,, ,, at 26°·66 (80° F.), 1·3545.
,, ,, at 37°·77 (100° F.), 1·7732.
,, ,, at 48°·88 (120° F.), 2·1812.

The increments of diffusibility, 0·3545, 0·4187, and 0·408 for equal increments of temperature, are probably affected by small errors of observation, but they appear to indicate that the diffusion increases at a higher, although not greatly higher, rate than the temperature. The average increase of diffusibility for the whole range of temperature observed is 0·03543, or $\frac{1}{28}$ for each degree (0·01969, or $\frac{1}{50}$ nearly for 1° F.).

The preceding experiments were made by diffusing a 2 per cent. solution of hydrochloric acid from wide-mouth phials immersed in a jar of water, as in my former experiments*. The times were observed in which an equal amount of the acid (0·777 gramme from three phials) was diffused out. These times of equal diffusion were 72 hours at 15°·55 (60° F.); 53·15 hours at 26°·63 (80° F.); 40·6 hours at 37°·77 (100° F.); and 39 hours at 48°·88 (120° F.).

Fig. 2.



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* Philosophical Transactions, 1850, p. 25.

The diffusate from a 2 per cent. solution of chloride of potassium in similar circumstances was 0·6577 gramme,

In 101·75 hours, at 15°·55 (60° F.); and
In 41·93 hours, at 48°·88 (120° F.).

The diffusate from a 2 per cent. solution of chloride of sodium was 0·6533 gramme,

In 124·75 hours, at 15°·55 (60° F.);
In 49·60 hours, at 48°·88 (120° F.).

In equal times the diffusate would be

For chloride of potassium	at 15°·55 (60° F.),	1
„ „	at 48°·88 (120° F.),	2·426
For chloride of sodium	at 15°·55 (60° F.),	1
„ „	at 48°·88 (120° F.),	2·5151.

As the ratio between the diffusates of hydrochloric acid, at the same two temperatures, was 1 to 2·1812, it appears that the acid is less increased in diffusibility than the salts at the higher temperature; chloride of sodium also is slightly more increased than chloride of potassium. The more highly diffusive the substance the less does it appear to gain by heat. Chloride of sodium appears to be sensibly 2½ times more diffusible at 48°·88 (120° F.) than at 15°·55 (60° F.): this gives an average increase of 0·014, or $\frac{1}{71}$ for 1 degree (0·025 for 1° F., or $\frac{1}{40}$). The inequality of diffusion which the three substances referred to exhibit at a low temperature, becomes therefore less at high temperatures; and it would appear to be the effect of a high temperature to assimilate diffusibilities. Heat, then, although it quickens the operation of diffusion, does not appear otherwise to promote the separation of unequally diffusive substances.

The results in such experiments are less disturbed by changes of temperature, if at all gradual, than might be supposed. A sensible separation was obtained of hydrochloric acid and chloride of sodium from each other, in a solution containing 2 per cent. of each substance, when the water-jar was heated up from 15°·55 to 95° C., in two hours, and maintained at the latter temperature during four hours more. Diffusion appeared to be accelerated about six times at the higher temperature.

At low temperatures, again, diffusion is proportionally slow.

The ratio of diffusibility of the following salts at two different temperatures appeared to be,—

For chloride of potassium at 5°·3 (41°·5 F.), 1 ; at 16°·6 (62° F.), 1·4413
For chloride of sodium at 5°·3 (41°·5 F.), 1 ; at 17°·4 (63°·4 F.), 1·4232
For nitrate of soda at 5°·3 (41°·5 F.), 1 ; at 17°·4 (63°·4 F.), 1·4475
For nitrate of silver at 5°·3 (41°·5 F.), 1 ; at 17°·4 (63°·4 F.), 1·3914

The salts are unequally affected to a sensible extent; and it will be observed that the superiority of chloride of potassium over chloride of sodium in diffusibility, is increased at the low temperature.

Within the range of temperature of the preceding experiments, the diffusibility of chloride of sodium being taken as 1 at 17°·4 (63°·4 F.), it becomes 0·7026 at 5°·3 (41°·5 F.); or it diminishes 0·0246, or $\frac{1}{40\cdot7}$, for a depression of 1° (0·0136, $\frac{1}{73\cdot5}$, for a depression of 1°F.).

3. *Dialysis.*

Passing from liquid diffusion in the water-jar, I may advert first to the diffusion of crystalloids through a gelatinous or colloid mass, the circumstance of the experiment being varied as little as possible from those of jar-diffusion.

Ten grammes of chloride of sodium and 2 grammes of the Japanese gelatin, or gelose of Payen, were dissolved together in so much hot water as to form 100 cub. cents. of liquid. Introduced into the empty diffusion-jar and allowed to cool, this liquid set into a firm jelly, occupying the lower part of the jar, and containing of course 10 per cent. of chloride of sodium. Instead of placing pure water over this jelly, it was covered by 700 cub. cents. of water containing 2 per cent. of the same gelose, cooled so far as to be on the point of gelatinizing, the jar at the same time being placed in a cooling mixture, in order to expedite that change. The jar with its contents was now left undisturbed for eight days at the temperature 10°. After the lapse of this time, the jelly was removed from the jar in successive portions of 50 cub. cents. each from the top, and the proportion of chloride of sodium in the various strata ascertained. The results were very similar to those obtained in diffusing the same salt in a jar of pure water. The diffusion in the gelose appeared more advanced in eight days than diffusion in water for seven days, as will be seen by comparing the gelose experiment below with a water experiment on chloride of sodium which had been conducted at nearly the same temperature (Table III).

TABLE XI.—Diffusion of a 10 per cent. solution of Chloride of Sodium in the jelly of gelose, for eight days, at 10°.

Number of stratum.	Diffusate, in grammes..	Diffusate from Table III.
1	·015	0·013
2	·015	0·017
3	·026	0·028
4	·035	0·051
5	·082	0·081
6	·130	0·134
7	·212	0·211
8	·350	0·318
9	·486	0·460
10	·630	0·640
11	·996	0·850
12	1·172	1·057
13	1·190	1·317
14	1·203	1·527
15 and 16	3·450	3·294
	9·992	9·998

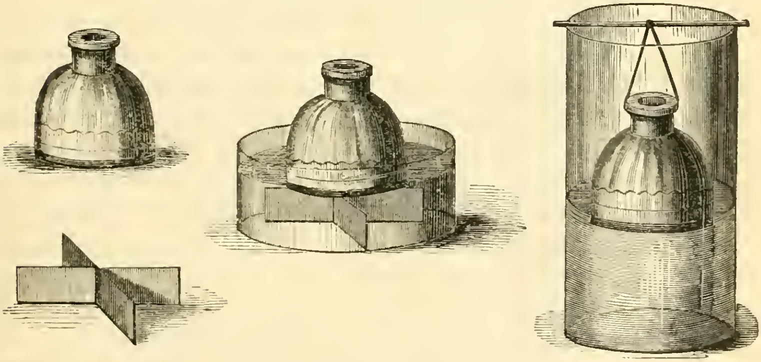
Diffusion of a crystalloid thus appears to proceed through a firm jelly with little or no abatement of velocity. With a coloured crystalloid, such as bichromate of potash, the gradual elevation of the salt to the top of the jar is beautifully illustrated. On the other hand, the diffusion of a coloured colloid such as caramel through the jelly, appeared scarcely to have begun after eight days had elapsed. The diffusion of a salt into the solid jelly may be considered as cementation in its most active form.

Numerous experiments were made on the diffusion of crystalloids through various dialytic septa, such as gelatinous starch, coagulated albumin, gum-tragacanth, besides animal mucus and parchment-paper, which all tended to prove how little the diffusive process was interfered with by the intervention of colloid matter. Salts appeared to preserve their usual relative diffusibility unchanged. The same partial separation of mixed salts was observed as in the water-jar. With a mixture, for instance, of equal parts of chlorides of potassium and sodium in a dialyser, the first tenth part of the mixture which passed through was found to consist of 59·17 per cent. of chloride of potassium and 40·83 per cent. of chloride of sodium. Double salts also, such as alum, and the sulphate of copper and potash, which admit of being resolved into pairs of unequally diffusive salts, were largely decomposed upon the dialyser, as they are in the water-jar. The effect of heat in promoting diffusion appeared, however, to be diminished in dialysis, at least with a parchment-paper septem. Thus the diffusion from a 2 per cent. solution of chloride of sodium in a constant period of three hours was,—

		Ratio.
At 10°	0.738 grm.	1
At 20	0·794 grm.	1·07
At 30	0·892 grm.	1·20
At 40	1·017 grm.	1·37

The rate of diffusion in water alone, without the septum, would have been doubled by an equal rise of temperature instead of being increased one-third only as above.

Fig. 3.—Bulb Dialyser.



The small glass bell-jar (fig. 3) formerly used as an osmometer, was conveniently applied to dialytic experiments. Two sizes of the bulb were employed, 3·14 and 4·44 inches in diameter respectively, and of which the dialytic septa possessed an area very nearly of $\frac{1}{100}$dth and $\frac{1}{200}$dth of a square meter (15·6 and 7·8 square inches). With 100 cub. cents. of fluid in the osmometer (the volume usually employed), the septum of the smaller instrument was covered to a depth of about 20 millimeters (0·8 inch), and the septum of the larger to a depth of 10 millimeters (0·4 inch). The thinner the stratum, the more exhaustive the diffusion in a given time. It is generally unadvisable to cover the septum deeper than 10 or 12 millimeters (half an inch), where a considerable diffusion is desired within 24 hours. The following practical observations may be found useful in applying the dialyser to actual cases of analysis. They refer to the parchment-paper septum, which is much the most convenient for use.

With a 2 per cent. solution of chloride of sodium, containing 2 grammes of the salt, and covering a septum of nearly 0·01 square meter (15·6 square inches) in area, to a depth of 10 millimeters, the salt which diffused in 5 hours amounted to 0·75 gramme, and in twenty-four hours to 1·657 gramme, leaving behind 0·343 gramme, or 17·1 per cent. of the original salt. The following experiments, made with the same osmometer and solution, show the effect of reducing the volume of liquid placed in the dialyser. The proportion of salt which diffused out in twenty-four hours was—

From 100 cub. cents. of solution 86 per cent.
From 50 cub. cents. of solution 92 per cent.
From 25 cub. cents. of solution 96 per cent.

In all cases the volume of water outside into which the salt escaped was ample, being from five to ten times greater than the volume of fluid placed in the dialyser, and it was changed during the continuance of the experiment. A much smaller volume of external water suffices, provided it is changed at intervals of a few hours. The temperature was 10° to 12°. It will be observed that these volumes correspond to a depth of liquid in the dialyser of 0·4, 0·2, and 0·1 inch respectively.

The time of travelling through the thickness of the parchment-paper itself may be observed, and is worthy of remark.

Of the quality of parchment-paper always used in these experiments, a square meter when dry, weighed 67 grammes; and when charged with water, 108·6 grammes. Taking the specific gravity of cellulose at 1·46, that of the lighter woods, the parchment-paper described will, in the humid state, have a thickness of 0·0877 millimeter, or $\frac{1}{11{\cdot}41}$ of a millimeter. Wet parchment-paper so thin is highly translucent. Gelatinous starch, slightly coloured with blue litmus, was applied by a brush to one side of the wet parchment-paper. Immediately afterwards a drop of water, containing $\frac{1}{1000}$dth part of *hydrochloric acid,* was applied on the point of the finger to the other (the lower) side of the paper.

The time required by the acid to affect the litmus, in five successive trials, was 6 seconds, 5·5 seconds, 6 seconds, and 5 seconds. The mean is 5·7 seconds, which is therefore the time required by hydrochloric acid, diluted already 1000 times, to travel a distance of 0·0877 of a millimeter, by the agency of diffusion. The temperature was 15°.

With hydrochloric acid diluted twice as much as before (water containing 0·0005 dry acid), the average time of passage was 10·4 seconds, or nearly double the preceding time.

Water containing $\frac{1}{1000}$dth of sulphuric acid (an acid less rapidly diffused than hydrochloric acid) reddened the litmus in 9·1 seconds, and when doubly diluted in 16·5 seconds.

These results are not effected, it is believed, by any sensible diffusive movement on the part of the litmus. The diffusion of that colouring matter, in a colloid medium, is so slow that it may be entirely disregarded. The acid, therefore, is not met in its way by the litmus, but really travels the entire distance expressed by the thickness of the parchment-paper. The first experiments related give a diffusive velocity, in water, to hydrochloric acid, already diluted one thousand times, of 0·0154 millimeter per second, and 0·924 millimeter in one minute.

The few following dialytic experiments may be recorded for the sake of the practical points which they bring out. They were made in the smaller osmometer, with 100 cub. cents. of a solution containing 10 grammes of each of the various substances. The area of the parchment-paper septum was 0·005 square meter, and the depth of the stratum of fluid placed upon it 20 millimeters. The substances diffused were all crystalloids, with the exception of gum-arabic.

The experiments were all made through the same portion of parchment-paper, and in the order of the Table; gum-arabic first, and chloride of sodium last. After every experiment, the bulb was immersed in water for twenty-four hours, to purify the septum, before it was again used. The diffusion of starch-sugar was repeated early and late in the series of experiments, with little change in the result, showing considerable uniformity in the action of the parchment-paper; the first diffusate of starch-sugar being 2 grammes, and the second 2·13 grammes. Yet the parchment-paper had been in contact with water or some solution for a whole fortnight between the two observations referred to.

Table XII.—Dialysis through Parchment-paper during twenty-four hours, at 10° to 15°.

Ten per cent. solutions.	Diffusate, in grammes.	Relative diffusate.	Osmose, in grammes of water.	Relative osmose.
Gum-arabie	0·029	·004	5·0	·263
Starch-sugar	2·000	·266	17·0	·894
Cane-sugar	1·607	·214	15·3	·805
Milk-sugar	1·387	·185	15·0	·789
Mannite	2·621	·349	17·6	·926
Glycerin	3·300	·440	17·6	·926
Alcohol	3·570	·476	7·6	·400
Starch-sugar (second experiment)	2·130	·284	16·8	·884
Chloride of sodium ..	7·500	1	19.0	1

A layer of animal mucus, taken from the stomach of the pig, 12 millimeters in thickness (10 grammes of humid mucus being spread over 0·005 square meter of surface), was applied, between two discs of calico, to the diffusion-bulb used above, the parchment-paper being first removed.

Table XIII.—Dialysis through Animal Mucus during twenty-five hours, at 10° to 15°.

Ten per cent. solutions.	Diffusate, in grammes.	Proportional diffusate.	Osmose, in grammes of water.
Gum-arabic	·023	·004	+29
Starch-sugar	1·821	·360	+ 7·6
Cane-sugar	1·753	·347	+ 4·6
Milk-sugar	1·328	·262	+ 7·1
Mannite	1·895	·375	+ 5·0
Alcohol	2·900	·573	+ 7·2
Starch-sugar	1·765	·349	+ 7·0
Glycerin	2·554	·505	+ 7·5
Chloride of sodium ..	5·054	1	− 0·2

The relative diffusibilities of the different substances present a considerable degree of similarity in the two Tables, and are equally analogous to the diffusibilities of the same substances observed in pure water. The intervention of a colloid septum cannot be said to have impeded much the diffusion of any of these substances except the colloid gum.

The dialysis through parchment-paper of several other organic substances, both crystalloids and colloids, may be brought together, in comparison with the chloride of sodium as a standard. The larger osmometer bulb was used, and the parchment-paper was now changed in each experiment. The substance in solution amounted to 2 grammes, the depth of fluid in the dialyser to 10 millimeters (0·4 of an inch), and the surface of the septum to 0·01 square meter (15·6 square inches).

Table XIV.—Dialysis through Parchment-paper during twenty-four hours, at 12°.

Two per cent. solutions.	Diffusate, in grammes.	Proportional diffusate.
Chloride of sodium	1·657	1·
Picric acid	1·690	1·020
Ammonia	1·404	·847
Theine	1·166	·703
Salicin	·835	·503
Cane-sugar	·783	·472
Amygdalin	·517	·311
Extract of quercitron	·305	·184
Extract of logwood	·280	·168
Catechu	·265	·159
Extract of cochineal	·086	·051
Gallo-tannic acid	·050	·030
Extract of litmus	·033	·019
Purified caramel	·009	·005

Picric acid and theine were actually diffused from 1 per cent. solutions, and the numbers observed are multiplied by 2. The crystallizable principles, thein, salicin, and amygdalin, appear greatly more diffusible than gallo-tannic acid, or than gum, as has been already seen. Such inequality of rate is likely to facilitate the separation of vegetable principles by the agency of dialysis.

4. *Preparation of Colloid Substances by Dialysis.*

The purification of many colloid substances may be effected with great advantage by placing them on the dialyser. Accompanying crystalloids are eliminated, and the colloid is left behind in a state of purity. The purification of soluble colloids can rarely be effected by any other known means, and dialysis is evidently the appropriate mode of preparing such substances free from crystalloids.

Soluble Silicic Acid.—A solution of silica is obtained by pouring silicate of soda into diluted hydrochloric acid, the acid being maintained in large excess. But in addition to hydrochloric acid, such a solution contains chloride of sodium, a salt which causes the silica to gelatinize when the solution is heated, and otherwise modifies its properties. Now, such soluble silica, placed for twenty-four hours in a dialyser of parchment-paper, to the usual depth of 10 millimeters, was found to lose in that time 5 per cent. of its silicic acid, and 86 per cent. of its hydrochloric acid. After four days on the dialyser, the liquid ceased to be disturbed by nitrate of silver. All the chlorides were gone, with no further loss of silica. In another experiment, 112 grammes of silicate of soda, 67·2 grammes of dry hydrochloric acid, and 1,000 cub. cents. of water were brought together, and the solution placed upon a hoop dialyser, 10 inches in diameter. After four days, the solution had increased to 1·235 cub. cents., by the action of osmose, colloid bodies being generally highly osmotic. The solution now gave no precipitate with nitrate of silver, and contained 60·5 grammes of silica, 6·7 grammes of that substance having been lost. The solution contained 4·9 per cent. of silicic acid.

The pure solution of silicic acid so obtained may be boiled in a flask, and considerably concentrated, without change; but when heated in an open vessel, a ring of insoluble silica is apt to form round the margin of the liquid, and soon causes the whole to gelatinize. The pure solution of hydrated silicic acid is limpid and colourless, and not in the least degree viscous, even with 14 per cent. of silicic acid. The solution is the more durable the longer it has been dialysed and the purer it is. But this solution is not easily preserved beyond a few days, unless considerably diluted. It soon appears slightly opalescent, and after a time the whole becomes pectous somewhat rapidly, forming a solid jelly transparent and colourless, or slightly opalescent, and no longer soluble in water. This jelly undergoes a contraction after a few days, even in a close vessel, and pure water separates from it. The coagulation of the silicic acid is effected in a few minutes by a solution containing $\frac{1}{10,000}$th part of any alkaline or earthy carbonate, but not by caustic ammonia, nor by neutral or acid salts. Sulphuric, nitric, and acetic acids do not coagulate silicic acid, but a few bubbles of carbonic acid passed through the solution produce that effect after the lapse of a certain time. Alcohol and sugar, in large quantity even, do not act as precipitants; but neither do they protect silicic acid from the action of alkaline carbonates, or from the effect of time in pectizing the fluid colloid. Hydrochloric acid gives stability to the solution: so does a small addition of caustic potash or soda.

This pure water-glass is precipitated on the surface of a calcareous stone without penetrating, apparently from the coagulating action of soluble lime-salts. The hydrated silicic acid then forms a varnish, which is apt to scale off on drying. The solution of hydrated silicic acid has an acid reaction, somewhat greater than that of carbonic acid. It appears to be really tasteless (like most colloids), although it occasions a disagreeable persistent sensation in the mouth, after a time, probably from precipitation.

Soluble hydrated silicic acid, when dried in the air-pump receiver, at 15°, formed a transparent glassy mass of great lustre, which was no longer soluble in water. It retained 21·99 per cent. of water after being kept two days over sulphuric acid.

The colloidal solution of silicic acid is precipitated by certain other soluble colloids, such as gelatin, alumina, and peroxide of iron, but not by gum or caramel. As hydrated silicic acid, after once gelatinizing, cannot be made soluble again either by water or by acids, it appears necessary to admit the existence of two allotropic modifications of that substance, namely, soluble hydrated silicic acid, and insoluble hydrated silicic acid, the fluid and pectous forms of this colloid.

The ordinary soluble silicate of soda is not at all colloidal, but diffuses as readily through a septum as the sulphate of soda does. Several crystalline hydrated silicates of soda are known (Fritzsche).

The amorphous silicic acid obtained by drying and calcining the jelly, and the vitreous acid obtained by igneous fusion, have both a specific gravity of about 2·2, according to H. Rose*, and appear to be the same colloidal substance; while the specific gravity of crystalloidal silicic acid (rock-crystal and quartz) is about 2·6.

Soluble silicic acid forms a peculiar class of compounds, which like itself are colloidal, and differ entirely from the ordinary silicates. The new compounds are interesting from their analogy to organic substances, and from appearing to contain an acid of greatly higher atomic weight than ordinary silicic acid. Like gallo-tannic acid, gummic acid, and the other organic colloidal acids, silicic acid combines with gelatin, the last substance appearing to possess basic properties. *Silicate of gelatin* falls as a flaky, white and opake precipitate, when the solution of silicic acid is gradually added to a solution of gelatin in excess. The precipitate is insoluble in water, and is not decomposed by washing. Silicate of gelatin prepared in the manner described, contains 100 silicic acid to about 92 gelatin. This is a greater proportion of gelatin than in the gallo-tannate of gelatin, and requires for soluble silicic acid a higher equivalent than that of gallo-tannic acid. In the humid state the gelatin of this compound does not putrefy.

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* Ann. Ch. Phys. [3], lvii. 163.

The acid reaction of 100 parts of soluble silicic acid is neutralized by 1·85 part of oxide of potassium, and by corresponding proportions of soda and ammonia. The *colli*-silicates or *co*-silicates thus formed are soluble and more durable than fluid silicic acid, but they are pectized by carbonic acid or by an alkaline carbonate, after standing for a few minutes. The co-silicate of potash forms a transparent hydrated film on drying *in vacuo*, which is not decomposed by water, and appears to require about ten thousand parts of water to dissolve it. The silicate of soda which Forchhammer obtained by boiling freshly precipitated silicic acid with carbonate of soda, and collecting the precipitate which falls on cooling, contains 2·74 per cent. of soda, and is represented by $NaO.36SiO_2$ (Gmelin). This silicate is probably a co-silicate of soda in the pectous condition. Soluble silicic acid produces a gelatinous precipitate in lime-water, containing 6 per cent. and upwards of the basic earth. This and the other insoluble earthy co-silicates appear not to be easily obtained in a definite state. They give out a more basic silicate to water on washing. The composition of these salts, and that also of the co-silicate of gelatin were found to vary according as the mode of preparation was modified. When a solution of gelatin was poured into silicic acid in excess, the co-silicate of gelatin formed gave, upon analysis, 100 silicic acid with 56 gelatin, or little more than half the gelatin stated above as found in the compound prepared by reversing the mode of mixing the solutions. The gallo-tannate of gelatin is known to offer the same variability in composition.

The gelatin used in the preceding experiments was isinglass (colle de poisson), purified by solution in hydrochloric acid and subsequent dialysis. When the acid escapes by diffusion, a jelly is formed in the dialyser. This jelly is free from the earthy matter, amounting to about 0·4 per cent. in isinglass, and is not liable to putrefaction.

Cosilicic acid also precipitates both *albuminic acid* and pure *casein*.

Soluble Alumina.—We are indebted to Mr. Walter Crum for the interesting discovery that alumina may be held in solution by water alone in the absence of any acid. But two soluble modifications of alumina appear to exist, alumina and metalumina. The latter is Mr. Crum's substance.

A solution of the neutral chloride of aluminium ($Al_2 Cl_3$), placed on the dialyser, appears to diffuse away without decomposition. But when an excess of hydrated alumina is previously dissolved in the chloride, the latter salt and free hydrochloric acid are found to escape by diffusion in a gradual manner, and the hydrated alumina, retaining little or no acid, to remain behind in a soluble state. A solution of alumina in chloride of aluminium, consisting at first of 52 parts of alumina to 48 of hydrochloric acid, after a dialysis of six days, contained 66·5 per cent. of alumina; after eleven days 76·5 per cent.; after seventeen days 92·4 per cent., and after twenty-five days the alumina appeared to be as nearly as possible free from acid, as traces only of hydrochloric acid were indicated by an acid solution of nitrate of silver. But in such experiments the alumina often pectizes in the dialyser before the hydrochloric acid has entirely escaped.

Acetate of alumina with an excess of alumina gave similar results. The alumina remained fluid in the dialyser for twenty-one days, and when it pectized was found to retain 3·4 per cent. of acetic acid, which is in the proportion of 1 equivalent of acid to 28·2 equivalents of alumina.

Soluble alumina is one of the most unstable of substances, a circumstance which fully accounts for the difficulty of preparing it in a state of purity. It is coagulated or pectized by portions, so minute as to be scarcely appreciable, of sulphate of potash and, I believe, by all other salts; and also by ammonia. A solution containing 2 or 3 per cent. of alumina was coagulated by a few drops of well-water, and could not be transferred from one glass to another without gelatinizing, unless the glass was repeatedly washed out by distilled water. Acids in small quantity also cause coagulation; but the precipitated alumina readily dissolves in an excess of the acid. The colloids gum and caramel also act as precipitants.

This alumina is a mordant, and possesses indeed all the properties of the base of alum and the ordinary aluminous salts. A solution containing 0·5 per cent. of alumina may be boiled without gelatinizing, but when concentrated to half its bulk, it suddenly coagulated. Soluble alumina gelatinizes when placed upon red litmus paper, and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol or by sugar. No pure solution of alumina, although dilute, remained fluid for more than a few days.

Like hydrated silicic acid, then, the colloid alumina may exist either fluid or pectous, or it has a soluble and insoluble form, the latter being the gelatinous alumina as precipitated by bases. It is evident that the extraordinary coagulating action of salts upon hydrated alumina must prevent the latter substance from ever appearing in a soluble state when liberated from combination by means of a base.

Colloidal alumina possesses also, I believe, a high atomic weight, like cosilicic acid. The chloride of aluminium with excess of alumina referred to above appears to be, either in whole or in part, a colloidal hydrochlorate of alumina, containing the latter substance with its large colloidal equivalent, and may be really neutral in composition. The soluble basic persalts, of iron, tin, &c. are likewise all colloidal, and have no doubt a similar constitution. Such colloidal salts are themselves slowly decomposed on the dialyser, being resolved into the crystalloidal acid which escapes and the colloidal oxide which remains behind.

Soluble Metalumina.—Mr. Crum first pointed out a singular relation of acetic acid to alumina, which has never been explained. Sulphate of alumina, when precipitated by acetate of lead or baryta, gives a *bin*acetate of alumina, with one equivalent of free acetic acid, the neutral teracetate of alumina not appearing to exist. It was further observed that, by keeping a solution of this binacetate in a close vessel at the boiling-point of water for several days, nearly the whole acetic acid came to be liberated, without any precipitation of alumina occurring at the same time. Mr. Crum boiled off the free acetic acid, or the greater part of it, and thus obtained his soluble alumina. The same result may be arrived at by dialysing a solution of acetate of alumina that has been altered by heat. In three days the acetic acid was reduced on the dialyser to 11 per cent., giving 1 equiv. acetic acid to 8 equivs. alumina; in six days to 7·17 per cent. acid; in thirteen days to 2·8 per cent. acid, or 1 equiv. acid to 33 equivs. alumina. The alumina exists in an allotropic condition, being no longer a mordant; and forming, when precipitated, a jelly that is not dissolved by an excess of acid. Metalumina resembles alumina in being coagulated by minute proportions of acids, bases, and of most salts. Mr. Crum found the solution of metalumina to require larger quantities of acetates, nitrates, and chlorides to produce coagulation than of sulphates. The solution of metalumina is tasteless, and entirely neutral to test-paper, according to my own observation.

Like alumina, the present colloid has therefore a fluid and a pectous form, the liquid soluble metalumina, and the gelatinous insoluble metalumina.

Soluble Peroxide of Iron.—A solution of hydrated peroxide of iron may be obtained by a process exactly analogous to that for soluble alumina. Perchloride of iron in solution is first saturated with hydrated peroxide of iron, added by small quantities at a time; or carbonate of ammonia may be added in a gradual manner to perchloride of iron, so long as the precipitated oxide continues to be redissolved on stirring. These red solutions of iron have lately been carefully investigated by Mr. Ordway (Silliman's Journal, [3], xxxix. 197), by M. Béchamp (Ann. Ch. Phys. [3], lvii. 293), and by M. Scheurer-Kestner (ibid. lv. 330). It is observed that the act of solution of the hydrated peroxide by the chloride of iron is a gradual process, demanding time. The quantity of oxide taken up will go on increasing for a long period, if digestion in the cold is continued. Mr. Ordway found chloride of iron to take up as much as 18 equivalents of peroxide of iron in the course of five months. This slowness of action is highly characteristic of colloids. Only monobasic acids, such as hydrochloric and nitric, serve for preparing such solutions, sulphuric and other polybasic acids giving insoluble subsalts with excess of ferric oxide, or of any other aluminous oxide. The red liquid so obtained is already a colloidal hydrochlorate of peroxide of iron, but requires to be dialysed for a sufficient time. Such a compound possesses an element of instability in the extremely unequal diffusibility of its constituents. Beginning with perchloride of iron, containing five or six equivalents of peroxide in solution, the whole solid matter also amounting to 4 or 5 per cent. of the liquid, and the latter forming a stratum of the usual depth of about half an inch in the dialyser, it was found that hydrochloric acid diffused out accompanied only by a small proportion of the iron. After eight days, the deep red solution in the dialyser contained peroxide of iron and hydrochloric acid, in the proportion of 97·6 per cent. of the former to 2·4 per cent. of the latter. In nineteen days the hydrochloric acid was reduced to 1·5 per cent., which gives 1 equiv. of acid to 30·3 equivs. peroxide of iron. The last solution was transferred to a phial, in which it remained fluid for twenty days, and then spontaneously pectized.

The peracetate of iron, prepared by double decomposition, is incapable of dissolving hydrated peroxide of iron, as is well known, but still may be made a source of soluble peroxide; as the salt referred to is itself decomposed to a great extent by diffusion on the dialyser. About one-half of the iron was lost by a diffusion of eighteen days, in a particular experiment, leaving on the dialyser a red liquid, in which ninety-four parts of peroxide of iron were still associated with six parts of acetic acid.

Water containing about 1 per cent. of hydrated peroxide of iron in solution has the dark red colour of venous blood. The solution may be concentrated by boiling to a certain point, and then pectizes. The red solution is coagulated in the cold by traces of sulphuric acid, alkalies, alkaline carbonates, sulphates and neutral salts in general, but not by hydrochloric, nitric, and acetic acids, nor by alcohol or sugar. The coagulum is a deep red-coloured jelly, resembling the clot of blood, but more transparent. Indeed the coagulation of this colloid is highly suggestive of that of blood, from the feeble agencies which suffice to effect the change in question, as well as from the appearance of the product. The coagulum formed by a precipitant, or in the course of time, without any addition having been made to the solution of peroxide of iron, is no longer soluble in water, hot or cold, but it yields readily to dilute acids. It is, in short, the ordinary hydrated peroxide of iron. Here then, again, we have a soluble and insoluble form of the same colloidal substance. Native hematite, which presents itself in mammillary concretions, is no doubt colloidal.

Soluble Metaperoxide of Iron.—The soluble peroxide of iron of M. Péan de Saint-Gilles* appears to be the analogue of metalumina. It was also prepared by the prolonged action of heat upon a pure solution of the acetate. The characteristic properties of this substance, which indicate its allotropic nature, are the orange-red colour and the opalescent appearance of its solution. The metaperoxide of iron is entirely precipitated of a brown ochreous appearance by a trace of sulphuric acid, or of an alkaline salt, and is insoluble in all cold acids, even when the latter are concentrated. The solubility of metaperoxide of iron in water appears to be more precarious, if possible, than that of the colloid alumina. It would no doubt be more safely prepared by diffusing away the acetic acid of the altered acetate of iron, than it is by boiling off that acid, as the solution is said to become precipitable by heat before the whole acetic acid is expelled.

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* Comptes rendus, 1855, vol. xl. p. 568.

Ferrocyanide of Copper.—Many of the insoluble ferrocyanides are crystalline precipitates, but the compound above named, and the different varieties of prussian blue, appear to be strictly colloidal.

Certain anomalous properties long observed in these compounds come thus to be explained. The ferrocyanide of copper precipitated from ferrocyanide of potassium and sulphate of copper, is a reddish-brown gelatinous precipitate, and carries down a portion of the potash salt. It is obtained of greater purity, like the other insoluble ferrocyanides, by the use of ferrocyanic acid as the precipitant. Ferrocyanide of copper is then darker in colour, and still more highly gelatinous. It is well known that this substance appears as a transparent almost colourless jelly, when precipitated from strong solutions. This colloidal matter assumes colour on the addition of water, in consequence of further hydration, following in this respect the analogy of the crystalloid salts of copper. The ferrocyanide of copper, when once precipitated, may be washed without loss, and exhibits no symptoms of solubility. But it has been remarked that the same salt, when produced by mixing the precipitating salts dissolved in not less than two or three thousand times their weight of water, gives a wine-red solution with no precipitate. This is the soluble condition of the colloid. When the red solution is placed in the dialyser, the salt of potash diffuses out, and the whole ferrocyanide of copper is retained behind in solution

Precipitated ferrocyanide of copper is not dissolved by oxalic acid, nor by oxalate of potash, but dissolves freely in about one-fourth of its weight of neutral oxalate of ammonia. The ferrocyanide of copper must be washed beforehand, to ensure solubility. A solution holding 3 or 4 per cent. of ferrocyanide of copper is of a dark reddish-brown colour, intermediate in tint between the acetate and meconate of iron. The solution is transparent, but assumes a peculiar appearance of opacity when seen by light reflected from its surface. The same appearance was observed by Péan de Saint-Gilles in his metaperoxide of iron.

When a red solution, such as that described, was dialysed, the oxalate of ammonia came away in a gradual manner; 30·6 per cent. of the oxalate of ammonia was found in the colourless diffusate of the first twenty-four hours, 31 per cent. of the same salt in the diffusate of the next three days, and 18·2 per cent. in the diffusates of the following seven days, making altogether 79·8 per cent., or four-fifths of the whole oxalate of ammonia originally introduced. A small portion of the ammoniacal salt is retained with force, as might be expected from a ferrocyanide. Although the diffusate appeared colourless, it was found to contain a little oxide of copper, namely, 0·041 gramme (of which 0·022 gramme diffused out in the first twenty-four hours), from 2 grammes of ferrocyanide of copper placed in the dialyser.

The liquid ferrocyanide of copper, both before and after being dialysed, may be heated without change, but it is pectized by foreign substances with extreme facility. This effect is produced by a minute addition of nitric, hydrochloric, and sulphuric acids in the cold, and of oxalic and tartaric acids with the aid of a slight heat. It is remarkable that acetic acid does not pectize the ferrocyanide of copper and many other colloids. Sulphate of potash, sulphate of copper, and metallic salts generally appear to pectize the red liquid. The oxalate of ammonia, if any is present, remains in solution.

Neutral Prussian Blue.—The blue precipitate from perchloride of iron and ferrocyanide of potassium, or ferrocyanic acid, is a bulky hydrate, which dries up into gummy masses, so far resembling a colloid. The precipitate dissolves readily with the aid of a gentle heat, in one-sixth of its weight of oxalic acid, giving the well-known solution of prussian blue, used as a blue ink. Prussian blue is equally soluble in the oxalate and binoxalate of potash. When the solution of prussian blue in oxalic acid was placed on the dialyser, no colouring matter came through, but 28 per cent. of the oxalic acid diffused away in the first twenty-four hours, accompanied by traces of peroxide of iron. The oxalic acid appears to leave the colloidal solution very slowly and incompletely, 8 per cent. diffusing away in the second twenty-four hours, 11 per cent. in the next four days, and 2 per cent. in the following six days. The colloidal solution of prussian blue was pectized by small additions of sulphate of zinc and several other metallic salts, but required larger quantities of the alkaline salts for precipitation.

Ferridcyanide of Iron.—The blue precipitate from the ferridcyanide of potassium and a protosalt of iron is soluble in oxalic acid and binoxalate of potash, but not in the neutral oxalates. This blue liquid is quite incapable of passing through the dialyser, and is equally colloidal with ordinary prussian blue. So also is *basic prussian blue* prepared by the spontaneous oxidation of precipitated ferrocyanide of protoxide of iron. This last colloid might probably be purified with advantage upon the dialyser.

The ammonio-tartrate of iron, ammonio-citrate of iron, and similar pharmaceutical preparations are chiefly colloidal matters.

Sucrate of Copper.—The deep blue liquid obtained by adding potash to a mixed solution of chloride of copper and sugar appears to contain a colloidal substance. Placed on a dialyser for four days, the blue liquid became green, and no longer contained either potassium or chlorine; it, in fact, consisted of oxide of copper united with twice its weight of sugar. The external liquid remained colourless, and gave no indication of copper when tested with sulphuretted hydrogen. The colloidal solution of sucrate of copper was sensitive in the extreme to pectizing agents. Salts and acids generally gave a bluish-green precipitate; even acetic acid had that effect. The precipitate, or pectous sucrate, after being well washed, consisted of oxide of copper with about half its weight of sugar, and is therefore a subsucrate. When the green liquid is heated strongly, it gives a bluish-green precipitate, and does not allow the copper to be readily reduced to the state of suboxide. The subsucrate of copper possesses considerable vivacity of colour, and might be used as a pigment. A solution of sucrate of copper absorbs carbonic acid from the air with great avidity.

The sucrate of copper dries up into transparent films of an emerald-green colour. These films are not altered in appearance or dissolved in cold or boiling alcohol. In water they are resolved into sugar and the pectous subsucrate of copper.

Sucrate of Peroxide of Iron.—The perchloride of iron with an addition of sugar is not precipitated by potash, provided the temperature is not allowed to rise. The peroxide of iron combined with the sugar is colloidal, and remains on the dialyser without loss. At a certain stage, however, the sugar appears to leave the peroxide of iron, and a gelatinous subsucrate of iron pectizes. The subsucrate of iron thrown down from the soluble sucrate by the addition of sulphate of potash, consisted of about 22 parts of sugar to 78 parts of peroxide of iron.

Sucrate of Peroxide of Uranium.—A similar solution may be obtained by adding potash to a mixture of the nitrate or chloride of uranium with sugar, avoiding heat. The solution is of a deep orange-yellow colour, and on the dialyser soon loses the whole of its acid and alkali. This fluid sucrate has considerable stability, but, like the sucrate of copper, is readily pectized by salts. The subsucrate pectized has considerable solubility in pure water.

Sucrate of Lime.—The well-known solution of lime in sugar forms a solid coagulum when heated. It is probably, at a high temperature, entirely colloidal. The solution obtained on cooling passes through the septum, but requires a much longer time than a true crystalloid like the chloride of calcium.

The blue solution of tartrate of copper in caustic potash contains a colloidal compound which has not been fully examined.

Soluble Chromic Oxide.—The definite terchloride of chromium, being a crystalloid, diffuses away entirely when placed in solution upon the dialyser. This salt, dissolves, with time, a certain portion of freshly precipitated hydrated chromic oxide, and becomes of a deeper green colour. Such a solution, after dialysis for twenty-two days, contained 8 hydrochloric acid to 92 chromic oxide; and after thirty days, 4·3 acid to 95·7 oxide, or 1 equiv. acid to 10·6 equivs. oxide. After thirty-eight days, the solution gelatinized in part upon the dialyser, and then contained 1·5 acid to 98·5 oxide, or 1 equiv. acid to 31·2 equivs. chromic oxide. This last solution, which may be taken to represent soluble chromic oxide, is of a dark green colour, and admits of being heated, and also of being diluted with pure water without change. It was gelatinized with the usual facility by traces of salts and other reagents which affect colloid solutions, and was then no longer soluble in water, even with the assistance of heat. It appeared to be the green hydrated oxide of chromium, as that substance is usually known. A metachromic oxide may possibly be obtained by heating and dialysing the acetate, but I have not attempted to form it.

Mr. Ordway succeeded in dissolving an excess of hydrated *uranic oxide* and of *glucina* in the chloride of uranium and of glucinum respectively. The dialysis of such solutions may be reasonably expected to yield soluble uranic oxide and soluble glucina.

It appears, then, that the hydrated peroxides of the aluminous type, when free, are colloid bodies; that two species of each of these hydrated oxides exist, of which alumina and metalumina are the types; one derived from an unchanged salt, and the other from the heated acetate of the base; further, that each of these species has two forms, one soluble and the other insoluble, or coagulated. This last species of duality should be well distinguished from the preceding allotropic variability of the same peroxide. The possession of a soluble and an insoluble (fluid and pectous) modification is not confined to hydrated silicic acid and the aluminous oxides, but appears to be very general, if not universal, among colloid substances. The double form is typified in the fibrin of blood.

The precipitated and gelatinous *peroxide of tin* is largely soluble in the bichloride of the same metal. Such a solution, when placed in the dialyser, allows the whole chlorine of the salt and a portion of the tin to diffuse away. Peroxide of tin or stannic acid remains behind, but not in a soluble state. It forms in the dialyser a semitransparent gelatinous cake, which after a few days is entirely free from chlorine. The original solution, containing excess of stannic acid, was diluted to various degrees, but was dialysed always with the same result. The coagulum was insoluble in hot or cold water, but dissolved readily in dilute acids. It was evidently the peroxide of tin unaltered.

The *metastannic acid*, or nitric acid peroxide of tin of Berzelius, forms a solid compound with a small quantity of hydrochloric acid. The compound is not dissolved by an excess of acid, but is soluble in pure water. The solution placed in the dialyser is readily decomposed, and leaves behind a semitransparent gelatinous mass of pure hydrated metastannic acid, insoluble both in water and acids. There appears, then, to be no soluble form of either hydrated stannic or metastannic acid, although both are colloidal substances.*

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* The soluble stannic and metastannic acids have since been obtained by dissolving the gelatinous substances above referred to in a small proportion of caustic potash; then neutralizing with acetic acid and dialysing again. The stannic or metastannic acid now remains fluid on the dialyser. Some alkali still adhering may be removed by the cautious addition of iodine dissolved in alcohol, the dialysis being continued. Stannic acid remains fluid when heated, but is converted into metastannic acid.—*Note by the Author.*

Precipitated *titanic acid* was dissolved in hydrochloric acid and submitted to dialysis. The hydrochloric acid readily diffused away, leaving hydrated titanic acid, gelatinous and insoluble, upon the dialyser. The proportion of titanic acid, which escaped from the dialyser and was lost, amounted to 0·050 gramme out of 2·5 grammes. Titanic acid thus resembles stannic acid in not presenting itself in the form of a fluid colloid.

Metallic protoxides are not soluble in their neutral salts, and cannot therefore be submitted to dialysis in the same conditions as the preceding peroxides. It was observed, however, that oxide of copper and oxide of zinc, when dissolved in ammonia, are capable of diffusing through a collodial septum, and are therefore not colloids themselves. The water outside the dialyser should be charged with ammonia in such an experiment.

5. *Dialysis of Organic Colloid Substances.*

Tannin.—The tannin employed was that extracted from gall-nuts by the ether process of Pelouze. A two per cent. solution of this substance, covering a surface of paper-parchment of the area of about $\frac{1}{100}$th of a square meter, or 15·6 square inches, to a depth of 10 millimeters, was diffused at 10° to 13° of temperature. The diffused matter amounted, in successive periods of twenty-four hours, to ·073, ·040, ·021, ·021, ·024 and ·024 gramme, derived from the two grammes in solution. Probably the earlier diffusates were increased by the presence of a little gallic acid, which, being a crystalloid, would no doubt be rapidly eliminated by diffusion. The latter observations indicate that tannin passes through a paper-parchment septum about 200 times less rapidly than chloride of sodium does in similar circumstances as to temperature and strength of solution. The diffusates from the tannin solution gave a precipitate with gelatin, and therefore contained tannin unaltered. But the diffusates probably contained also throughout some products of decomposition of a crystalloid character.

To the low diffusibility of tannin may be ascribed the remarkably slow penetration of skins by that substance in the ordinary operation of tanning leather. Tannin appears to form compounds of much stability with certain other colloids, as tanno-gelatin, and the compound with albumin which appears to be the primary basis of the vegetable cell (Fremy).

Gum.—The diffusate obtained from a solution containing 2 grammes of gum-arabic, in experiments corresponding in their conditions with the experiments upon tannin just related, was ·013 gramme per day. The power of gum to penetrate the colloid septum appears, therefore, to be one-half less than that of tannin, and 400 times less than the diffusibility of chloride of sodium. Gum gave the same amount of diffusate with a mucous septum as with parchment-paper. When substances of the crystalloid class are mixed with the gum, the diffusion of the latter appears to be still further reduced, and may even be entirely extinguished. The separation of colloids from crystalloids by dialysis is, in consequence, generally more complete than might be expected from the relative diffusibility of the two classes of substances.

Vegetable gum, which Fremy has shown to be a gummate of lime, can be purified by a dialytic method, which may be found applicable with advantage in other cases. Oxalic acid, it is known, precipitates lime from the gum very imperfectly. Hydrochloric acid may be used to separate that base from a solution of gum placed upon the dialyser, with more effect. It is only necessary to add to a strong solution of gum 4 or 5 per cent. of hydrochloric acid, and to dialyse till the gum-solution gives no precipitate with nitrate of silver. In an experiment made upon a 20 per cent. solution of gum, the ash was reduced to 0·1 per cent. of the gum in five days. The gummic acid possesses a sensible acid reaction, about equal to that of carbonic acid. This acid reaction was neutralized, in 100 parts of gummic acid, by 2·85 parts of potash. This amount of potash is very nearly equivalent to the lime originally present in the gum (1·72 lime, or 3·07 carbonate of lime, being equivalent to 2·89 potash). When the gummate of potash itself was dialysed without addition, the potash gradually diffused away, possibly in the state of carbonate, and left the gum again possessed of an acid reaction. Gummic acid, well dried at 100°, becomes insoluble in water, but swells up in that liquid, like gum-tragacanth. We appear to have here the pectous form of gummic acid.

It is worthy of inquiry whether such native gums as are insoluble in water are not the pectous forms of soluble gum, rather than allotropic varieties of that substance. So also of the metagummic acid of Fremy, formed by the action of strong sulphuric acid on mucilage. This last substance is insoluble in water, but was found by Fremy to afford, when neutralized by lime and alkalies, a soluble gum undistinguishable from gum-arabic.

Gummic acid produces a remarkable compound with gelatine. When solutions of these two colloids are mixed, oily drops fall and form a nearly colourless jelly on standing. This jelly is very fusible, melting at 25°, or by the heat of the hand. The *gummate of gelatin* may be washed slightly without decomposition, but is soluble to a certain extent in pure water, and still more so in a solution of gelatine. Prepared with gummic acid in excess, the compound, when dried at 100°, consisted of 100 gummic acid with 59 gelatin. The drops and the jelly contained 83·5 per cent. of water. Solution of gelatin is not precipitated by unpurified gum, nor by the gummate of potash.

Dextrin.—A two per cent. solution of dextrin, prepared from starch, was diffused in the same conditions as the preceding substances, but through a mucus septum. It gave in twenty-four hours ·034 gramme of diffusate from 2 grammes, or about three times more diffusate than was given by gum-arabic.

Caramel.—The dialytic examination of this substance adds to the accurate information on the subject lately supplied by M. A. Gélis*, and places caramel indisputably in the colloid class. The crude caramel obtained by heating cane-sugar at 210°—220°, when placed on the dialyser, allows certain intermediate coloured substances (Caramelane and Caramelene of Gélis) to diffuse out with considerable facility, while the compound containing the largest proportion of carbon remains behind. The latter substance, as obtained by me, possessed five times the colouring power of the original crude caramel, weight for weight. This highest soluble member of the caramel series may also be obtained, more quickly, by precipitation from its aqueous solution by means of alcohol. But I found it necessary to repeat the precipitation four times, or till the mass thrown down, from being plastic at first became pulverulent. A solution containing 10 per cent. of the caramel so purified was gummy; and on standing, it formed a tremulous jelly entirely soluble in hot or cold water. Evaporated *in vacuo*, the solution dries up into a black shining mass, which is tough and elastic, while it still possesses a certain proportion of water, like gum containing some water. Once thoroughly dried at a low temperature, this soluble caramel may be heated, afterwards, to 120° and retain complete solubility. But if a solution of the same caramel be directly evaporated to dryness by the heat of a water-bath, the whole matter is rendered insoluble in hot or cold water. The soluble and insoluble caramel have the same composition, and appear to illustrate the usual double form of colloids. The proportion of carbon in the fluid caramel was found as high as 54·59 per cent., which comes nearer to $C_{24} H_{13} O_{13}$ (requiring C 55·17) than any other formula in which the oxygen and hydrogen are assumed to be present in the proportion of water. In the analysis by Gélis of his caramelin, the proportion of carbon did not exceed 51·33 per cent., which does not apply to the present substance.

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* Ann. Ch. Phys. [3], lii, 352.

Fluid caramel is wholely tasteless, and appears to be neutral. It exhibits the same excessive sensibility to crystalloidal reagents which is witnessed in fluid silicic acid and alumina. The solution is precipitated or pectized by mere traces of any mineral acid, by alkaline sulphates, chloride of sodium, by most other salts, and by alcohol. The caramel then forms a brownish black pulverulent substance, insoluble in hot or cold water. The presence of sugar and of the intermediate brown substances protects fluid caramel in a remarkable way from the action of crystalloids, and accounts for the preceding properties not being observed in crude caramel. This colloid appears also to be precipitated by certain substances of its own class, such as peroxide of iron.

Pectous caramel may readily have its solubility restored. Placed in dilute potash, the caramel swells and appears gelatinous, and is dissolved on the application of heat. When this solution is dialysed, the potash is quickly reduced to the proportion of about 9 per cent., which forms a neutral compound. If an excess of acetic acid be now added, the whole potash is soon diffused away, and pure soluble caramel remains on the dialyser. Even carbonic acid will carry away the potash.

The extremely low diffusibility which has been assigned to caramel in former Tables, belongs to that substance as last described; the brown intermediate substances which accompany it in crude caramel are considerably more diffusive, although they again are much less diffusive than any variety of crystallizable or uncrystallizable sugar. When the molasses of the cane-sugar are diffused, much the greater portion of the colouring matters remains in the dialyser.

With the parchment-paper septum the fluid caramel appeared even less dialysable than gum, the diffusate in twenty-four hours from a 2 per cent. solution of the former being ·009 gramme only, while that of the latter was ·013. Caramel may be stated, approximately, to be 600 times less dialysable than chloride of sodium, and 200 times less so than sugar. Hence liquids coloured with caramel, such as porter and coffee, may be dialysed for a day with the passage of very little colouring matter.

Before leaving caramel, the analogy may be referred to which the insoluble form of that substance presents to *coal*. Caramelization appears the first step in that direction,—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages.

Albumin.—The purification of albumin is effected with much advantage upon the dialyser. The solution of egg-albumin is mixed freely with acetic acid and then dialysed. The earthy and alkaline salts are speedily got rid of, and in three or four days the albumin burns without leaving a trace of ash. Although the acetic acid used in the process appears to diffuse off entirely, albumin prepared in the manner described has a faint acid reaction. It also coagulates milk when mixed with the latter and heated. Albumin so prepared retains its constituent sulphur.

The passage through parchment-paper of pure albumin prepared by the unobjectionable process of M. Wurtz is so slow, that several days are required to produce a sensible result. Thus the diffusate from a solution of 2 grammes of albumin in 50 grammes of water was 0·052 gramme in eleven days, which gives 0·005 gramme in a single day. Albumin, then, appears to be about 2½ times less dialysable than gum, and 1,000 times less so than chloride of sodium.

Even combination with an alkali does not appear to enable albumin to pass through the colloid septum. To half a gramme of pure albuminic acid dissolved in 50 grammes of water, ·05 gramme of hydrate of soda was added (one-tenth of the weight of the albumin), and the liquid was placed upon parchment-paper. No albumin could be discovered in the diffusate of several days, but it gave ·069 gramme of carbonate of soda, equivalent to ·053 gramme of hydrate of soda; that is the whole soda originally added to the albumin. The separation of the soda from the albumin may possibly have been aided by the presence of carbonic acid in the water, but certainly the entire separation of the alkali from albumin by diffusion through a colloidal film is a remarkable fact. Hydrate of potash was found to diffuse away from albumin in the same manner.

A solution of *Emulsin* is precipitated by albuminic and gummic acids, but not by unpurified albumin or gum-arabic. The precipitates are white and opaque, pulverulent, and not gelatinous. They are soluble in acetic acid.

A thin stratum of pure albumin coagulated by heat appears to intercept completely the passage of liquid albumin of the egg. Forty grammes of undiluted egg-albumin, representing 5·6 grammes of dry albumin, were placed on a dialyser of the small size, composed of two sheets of calico well-impregnated with albumin and coagulated by heat of steam, as in the albuminized osmometer*. After twelve days the volume of liquid within the instrument had increased to 117 grammes by osmose, while a diffusate had passed through the dialyser of 0·243 gramme, or 4·34 per cent. of the original dry albumin. This diffusate consisted of salts chiefly, with some organic matter, but no portion of the latter was coagulable by heat.

Neither gelatinous starch, animal gelatin dissolved in water, nor extract of flesh, appears to be capable of diffusing through a colloid septum in a sensible degree, although salts and other crystallizable substances, which are mixed with the former, diffuse through the septum readily, and may thus be separated from the former substances.

6. *Separation of Arsenious Acid from Colloidal Liquids.*

Dialysis may be advantageously applied to the separation of arsenious acid and metallic salts from organic solutions in medico-legal inquiries. The process has the advantage of introducing no metallic substance or chemical reagent of any kind into the organic fluid. The arrangement for operating is also of the simplest nature.

The organic fluid is placed, to the depth of half an inch, on a dialyser formed of a hoop of gutta percha 10 or 12 inches in diameter, covered with parchment-paper (fig. 1, page 220). The dialyser is then floated in a basin containing a volume of water about four times greater than the volume of organic fluid in the dialyser. The water of the basin is generally found to remain colourless after the lapse of twenty-four hours, and after being concentrated by evaporation, it admits of the application of the proper reagents to precipitate and remove a metal from solution.

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* Philosophical Transactions, 1854, p. 189.

One-half to three-fourths of the crystalloidal and diffusible constituents of the organic fluid will generally be found in the water of the basin.

In the few illustrative experiments which follow, the 4-inch bulb dialyser, having an area of 16 square inches, or about $\frac{1}{100}$dth part of a square meter, was generally made use of (fig. 3, page 239). The volume of liquid placed in the bulb was 50 cubic centimeters, and accordingly covered the dialyser to a depth of 5 millimeters, or about 0.2 inch. The outer volume of water (in the jar) was not less than 1 litre, or twenty times the volume of the solution on the dialyser.

1. A solution of arsenious acid, in pure water, was first placed on the dialyser, the water containing 0·5 per cent. of arsenious acid, or 0·25 gramme of that substance, for twenty-four hours. The dialyser being then removed, the outer fluid was concentrated by heat, and then precipitated by sulphuretted hydrogen. It gave 0·300 gramme of tersulphide of arsenic, equivalent to 0·241 gramme of arsenious acid. It appears, then, that about 95 per cent. of the arsenious acid had diffused from the dialyser into the water-jar in twenty-four hours.

2. Water, with one-fourth of its volume of fluid egg-albumin and 0·25 gramme, or 0·5 per cent. of arsenious acid, was now placed on the dialyser as before. The diffusate gave, with sulphuretted hydrogen, after being acidulated with hydrochloric acid, 0·267 gramme of tersulphide of arsenic, equivalent to 0·214 gramme of arsenious acid.

3. The water contained 10 per cent. of gum-arabic and 1 per cent. arsenious acid, the latter amounting to 0·5 gramme. From the diffusate was derived 0·505 gramme of tersulphide of arsenic, equivalent to 0.406 gramme of arsenious acid. The dialyser still gave out arsenious acid when immersed for a second day in water. The outer fluid contained no gum.

It may be added that a similar 1 per cent. solution of arsenious acid, without the gum, gave a diffusate of 0·45 gramme arsenious acid in the same time, that is, nine-tenths of the whole acid.

4. A solution in hot water of 1 per cent. isinglass and 0·5 per cent. of arsenious acid (0·25 gramme), formed a jelly upon the dialyser on cooling. The diffusate from the jelly gave 0·260 tersulphide of arsenic, equivalent to 0·209 arsenious acid, with no gelatine. The escape of the arsenious acid appears then to have been slightly retarded by the fixing of the gelatinous solution.

This is probably due to the arrest of mechanical movement within the gelatinous stratum, and not to any sensible impediment offered by the jelly to diffusion.

In another experiment, similar to the last, but continued for four days instead of twenty-four hours, the tersulphide of arsenic weighed 0·320 gramme, equivalent to 0·257 arsenious acid.

5. A quantity of white of egg, amounting to 50 grammes, to which 0·01 gramme of arsenious acid in solution had been added, was coagulated by heat. The solid mass was then cut up into small pieces and placed on the dialyser, mixed with 50 grammes of water; after the usual period of twenty-four hours, the diffusate gave 0·01 gramme of tersulphide of arsenic, equivalent to 0·008 gramme arsenious acid. Here, of the mass upon the dialyser, the arsenious acid formed only $\frac{1}{10,000}$dth part, yet four-fifths of it were recovered.

6. One hundred grammes of milk, charged with $\frac{1}{10,000}$dth part of arsenious acid (0·01 gramme), and forming a stratum on the dialyser of 10 millimeters, gave a diffusate which yielded 0·010 tersulphide of arsenic, equivalent to 0·008 gramme of arsenious acid. The outer liquid was colourless, and gave no indication of casein, but it contained of course the salts and the sugar of the milk.

7. The same experiment was repeated with sized writing-paper, as the septum, applied to the same bulb. The result was a slight increase in the quantity of arsenious acid recovered.

It appears, then, that arsenious acid separates on the dialyser from gum, from gelatine, albumin, fluid or coagulated, and from casein, and is obtained in a solution fit for the application of reagents.

8. Half a litre of dark-coloured porter, with 0·05 gramme of arsenious acid added ($\frac{1}{10,000}$dth part of arsenious acid) was placed on a hoop dialyser, 8 inches in diameter, and the whole floated in an earthenware basin containing two or three litres of water. After twenty-four hours, the latter fluid had acquired a slight tinge of yellow. It yielded, when concentrated and precipitated by sulphuretted hydrogen, upwards of one-half of the original arsenious acid in a fit state for examination.

9. In a similar experiment on 200 grammes of defibrinated blood charged with $\frac{1}{4000}$dth part of arsenious acid (0·05 gramme), and placed in a similar dialyser to the last for twenty-four hours,

the diffusate of arsenious acid was recovered with the same facility, and appeared to be equally considerable.

10. Animal intestines, charged with the usual minute proportion of arsenious acid, were cut into small pieces and digested in water, about 32° C., for twenty-four hours. The whole was then thrown upon a dialyser for an equal time. Arsenious acid diffused out so free from colloidal matter that the action of reagents was not interfered with. A high temperature in digesting the intestines is quite unnecessary, and appeared indeed to increase the difficulty of diffusing out the arsenious acid afterwards.

The *tartrate of potash and antimony*, mixed in a small proportion of $\frac{1}{10,000}$dth, with defibrinated blood and with milk, was separated by dialysis quite as effectually as arsenious acid above.

Strychnine also was separated from organic fluids in the same manner, a small addition of hydrochloric acid being first made to the fluid on the dialyser.

Dialysis then appears of general application in the preparation of a liquid for examination by chemical tests, whether the poison looked for be mineral or organic. All soluble poisonous substances, whatever their origin, appear to be crystalloids, and accordingly pass through collodial septa.

7. *Colloidal Condition of Matter.*

I may be allowed to advert again to the radical distinction assumed in this paper to exist between colloids and crystalloids in their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass.

The colloidal character is not obliterated by liquefaction, and is therefore more than a modification of the physical condition of solid. Some colloids are soluble in water, as gelatin and gum-arabic; some are insoluble, like gum-tragacanth. Some colloids, again, form solid compounds with water, as gelatin and gum-tragacanth, while others, like tannin, do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes, notwithstanding their differences.

The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow, time indeed appearing essential to all colloidal changes. The change of temperature, usually occurring in the act of solution, becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced and precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents, as has already been explained.

While soluble crystalloids are always highly sapid, soluble colloids are singularly insipid. It may be questioned whether a colloid, when tasted, ever reaches the sentient extremities of the nerves of the palate, as the latter are probably protected by a colloidal membrane, impermeable to soluble substances of the same physical constitution.

It has been observed that vegetable gum is not digested in the stomach. The coats of that organ dialyse the soluble food, absorbing crystalloids and rejecting all colloids. This action appears to be aided by the thick coating of mucus which usually lines the stomach.

The secretion of free hydrochloric acid during digestion—at times most abundant—appears to depend upon processes of which no distinct conception has been formed. But certain colloidal decompositions are equally inexplicable upon ordinary chemical views. To facilitate the separation of hydrochloric acid from the perchloride of iron, for instance, that salt is first rendered basic by the addition of peroxide of iron. The comparatively stable perchloride of iron is transformed, by such treatment, into a feebly-constituted colloidal hydrochlorate. The latter compound breaks up under the purely physical agency of diffusion, and divides on the dialyser into colloidal peroxide of iron and free hydrochloric acid. The super-induction of the colloidal condition may possibly form a stage in many analogous organic decompositions.

A tendency to spontaneous change, which is observed occasionally in crystalloids, appears to be general in the other class. The fluid colloid becomes pectous and insoluble by contact with certain other substances, without combining with these substances, and often under the influence of time alone. The pectizing substance appears to hasten merely an impending change. Even while fluid a colloid may alter sensibly, from colourless becoming opalescent; and while pectous the degree of hydration may become reduced from internal change. The gradual progress of alteration in the colloid effected by the agency of time, is an investigation yet to be entered upon.

The equivalent of a colloid appears to be always high, although the ratio between the elements of the substance may be simple. Gummic acid, for instance, may be represented by $C_{12} H_{11} O_{11}$, but judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule.

With silicic acid, which can exist in combination both as a crystalloid and colloid, we have two series of compounds, silicates and cosilicates, the acid of the latter appearing to have an equivalent much greater (thirty-six times greater in one salt) than the acid of the former. The apparently small proportion of acid in a variety of metallic salts, such as certain red salts of iron, is accounted for by the high colloidal equivalent of their bases. The effect of such an insoluble colloid as prussian blue in carrying down small proportions of the precipitating salts, may admit of a similar explanation.

Gelatin appears to hold an important place as a colloidal base. This base unites with colloidal acids, giving a class of stable compounds, of which tanno-gelatin only appears to be hitherto known. Gelatin is precipitated entirely by a solution of metaphosphoric acid added drop by drop, 100 parts of gelatin uniting with 3·6 parts of the acid. The compound formed is a semitransparent, soft, elastic, and stringy solid mass, presenting a startling resemblance to animal fibrin. It will be an interesting inquiry whether metaphosphoric acid is a colloid, and enters into the compound described in that character, or is a crystalloid, as the small proportion and low equivalent of the acid would suggest. Gelatin is also precipitated by carbolic acid.

The hardness of the crystalloid, with its crystalline planes and angles, is replaced in the colloid by a degree of softness, with a more or less rounded outline. The water of crystallization is represented by the water of gelatination. The water in gelatinous hydrates is aptly described by M. Chevreul as retained by "capillary affinity," that is, by an attraction partaking both of the physical and chemical character. While it is here admitted that chemical affinity of the lowest degree may shade into capillary attraction, it is believed that the character of gelatinous hydration is as truly chemical as that of crystalline hydration. Combination of a colloid with water is feeble, it is true, but so is combination in general with the colloid. Notwithstanding this, anhydrous colloids can decompose certain crystalloid hydrates. The water in alcohol of greater strength than corresponds with the density 0·926, which represents the definite hydrate $C_4H_6O_2+6\,HO$, is certainly in a state of chemical union. But alcohol so high as 0·906, contained in a close vessel, is concentrated in a notable degree by contact with dry mucus, gelatin, and gum, and sensibly even by dry parchment-paper. Dilute alcohol divided from the air of the atmosphere by a dry septum of mucus, gelatin, or gum, is also concentrated by evaporation, as it is in the well-known bladder experiment of Sömmering. The selective power is here apparent of the colloid for water, that fluid being separated from alcohol, and travelling through the colloidal septum by combination with successive molecules of the latter, till the outer surface is reached and evaporation takes place. The penetration in this manner of a colloid by a foreign substance may be taken as an illustration of the phenomena of cementation. Iron and other substances which soften under heat, may be supposed to assume at the same time a colloidal constitution. So it may be supposed does silica when fused into a glass by heat; and every other vitreous substance.

Gelatinous hydrates always exhibit a certain tendency to aggregation, as is seen in the jelly of hydrated silicic acid and of alumina. With some the jelly is also adhesive, as in glue and mucus. But unless they be soluble in water, gelatinous hydrates, when once formed, are not always adhesive. Separated masses do not reunite when brought into contact. This want of adhesiveness is very remarkable in the gelose of Payen, which resembles gelatin so closely in other respects. Layers of a gelose solution, allowed to cool and gelatinize in succession in a diffusion-jar (p. 199), do not adhere together.

Ice itself presents colloidal characters at or near its melting-point, paradoxical although the statement may appear. When ice is formed at temperatures a few degrees under 0°C., it has a well-marked crystalline structure, as is seen in water frozen from a state of vapour, in the form of flakes of snow and hoar-frost, or in water frozen from dilute sulphuric acid, as observed by Mr. Faraday. But ice formed in contact with water at 0°, is a plain homogeneous mass with a vitreous fracture, exhibiting no facets or angles. This must appear singular when it is considered how favourable to crystallization are the circumstances in which a sheet of ice is slowly produced in the freezing of a lake or river. The continued extrication of latent heat by ice as it is cooled a few degrees below 0°C., observed by M. Person, appears also to indicate a molecular change subsequent to the first freezing. Further, ice, although exhibiting none of the viscous softness of pitch, has the elasticity and tendency to rend seen in colloids. In the properties last mentioned, ice presents a distant analogy to gum incompletely dried, to glue, or any other firm jelly. Ice further appears to be of the class of adhesive colloids. The redintegration (regelation of Faraday) of masses of melting ice, when placed in contact, has much of a colloid character. A colloidal view of the properties of ice indicated in the glacier movement will readily develope itself.

A similar extreme departure from its normal condition appears to be presented by a colloid holding so high a place in its class as albumin. In the so-called blood-crystals of Funke, a soft and gelatinous albuminoid body is seen to assume a crystalline contour. Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute?

8. *Osmose.*

Little has been said in the present paper respecting osmose, a subject closely connected with colloidal septa. It now appears to me that the water movement in osmose is an affair of hydration and of dehydration in the substance of the membrane or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic result, otherwise than as it affects the state of hydration of the septum.

Osmose is generally considerable, through membranous and other highly hydrated septa, with the solution of any colloid (gum, for instance) contained in the osmometer. Yet the diffusion outwards of the colloid is always minute, and may sometimes amount to nothing. Indeed, an insoluble colloid, such as gum-tragacanth, placed in powder within the osmometer, was found to indicate the rapid entrance of water, to convert the gum into a bulky gelatinous hydrate. Here no outward or double movement is possible.

The degree of hydration of any gelatinous body is much affected by the liquid medium in which it is placed. This is very obvious in fibrin and animal membrane. Placed in pure water, such colloids are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose. The contact of the saline fluid is thus attended by a continuous catalysis of the gelatinous hydrate, by which it is resolved into a lower gelatinous hydrate and free water. The inner surface of the membrane of the osmometer contracts by contact with the saline solution, while the outer surface dilates by contact with pure water. Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose, by equalizing the condition as to saline matter of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmose, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum.

The substances fibrin, albumin, and animal membrane swell greatly when immersed in water containing minute proportions of acid or of alkali, as is well known. On the other hand, when the proportion of acid or alkali is carried beyond a point peculiar to each substance, contraction of the colloid takes place. Such colloids as have been named acquire the power of combining with an increased proportion of water, and of forming superior gelatinous hydrates, in consequence of contact with dilute acid or alkaline reagents. Even parchment-paper is more elongated in an alkaline solution than in pure water. When so hydrated and dilated, the colloids present an extreme osmotic sensibility. Used as septa, they appear to assume or resign their water of gelatination under influences apparently the most feeble. It is not attempted to explain this varying hydration of colloids with the osmotic effects thence arising. Such phenomena belong to colloidal chemistry, where the prevailing changes in composition appear to be of the kind vaguely described as catalytic. To the future investigation of catalytic affinity, therefore, must we look for the further elucidation of osmose.

XXXVI.—*On the Composition of the Aqueous Acids of Constant Boiling Point.—Second Communication.*

By Henry Enfield Roscoe.

In a paper published in volume XIII of the *Quarterly Journal of the Chemical Society*, I showed that the acid liquids of constant composition obtained by distilling, under the ordinary atmospheric pressure, aqueous acids of very different degrees of strength, cannot be regarded as definite chemical combinations of acid and water, because, in the first place, their constituents are not, with one fortuitous exception, contained in simple atomic proportions; and, secondly, because these acid liquids undergo a gradual alteration in composition when exposed to a gradual alteration of physical condition, such as change of the temperature of ebullition.

I proved, on distilling aqueous sulphuric, nitric, hydrochloric, hydrobromic, hydriodic, and hydrofluoric acids of various strengths at different temperatures, that for every temperature each acid attains a particular constant composition and reaches a fixed boiling point; and I concluded that in these cases the resulting composition is determined rather by physical than by chemical attractions. I have since, likewise shown* that aqueous perchloric acid comports itself on distillation in an analogous manner. I have now to add

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[*] "On Perchloric Acid and its hydrates."—Proceedings of the Royal Society, vol. xi, p. 493.

to these results a description of the phenomena attending the distillation of aqueous formic and acetic acids.

1. *Formic Acid.*

According to Liebig,* an aqueous formic acid containing one atom of water ($H_2\Theta$) to two atoms of real acid ($\text{Ȼ}H_2\Theta_2$), and boiling at the fixed temperature of 106°C., is obtained by distilling 18 parts of formate of lead with 6 parts of oil of vitriol and 1 part of water, the real acid, according to the same chemist, boiling at 98°·5 C. In order to obtain further evidence respecting the composition of this aqueous acid of constant boiling point, pure glacial formic acid was prepared by decomposing formate of lead with dry sulphuretted hydrogen and rectification over an excess of the dry lead-salt. The boiling point of the acid thus obtained was found by Kopp's method to be 101°·1 C. under a pressure of 758 mm. of mercury†. The first portions of the distillate were solidified, and after one-third of the glacial acid had been removed by melting, the residue was analysed with standard soda, and found to contain 100·2 per cent. of pure formic acid. Another portion of the same acid was distilled to one-fifth of its volume, and the residue analysed, first by soda and secondly by neutralization with pure carbonate of barium, the barium in solution being estimated as sulphate. According to the soda analysis, the substance contained 100·0 per cent. of formic acid; according to the barium determination, it contained 99·72 per cent.

The pure acid was mixed with water in different proportions, the liquids distilled under the ordinary atmospheric pressure to a known fraction of their original bulk, and the composition of the residue determined. From a series of experiments thus made, it appears that a liquid containing 77·5 parts of acid to 22·5 parts of water undergoes no change by distillation under a pressure of 760 mm. of mercury, boiling at the fixed temperature of 107°·1 C.; and that all mixtures containing more acid or more water than this quantity, when distilled under the above conditions, ultimately attain this same fixed boiling point and constant composition. The following table contains the results of the experiments:—Column I. gives the volume of liquid employed; column II. the percentage of real acid contained in this liquid; column III.

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* Handwörterbuch der Chemie, 1842. Article "Ameisensäure."

† It is remarkable that Kopp gives the boiling point of pure formic acid at 105°·3 C under a pressure of 760 mm.

the volume of liquid remaining after distillation; column IV. the percentage of real acid contained in the residual liquid.

I.—Distillation of Aqueous Formic acid under the ordinary atmospheric pressure.

No.	I.	II.	III.	IV.	No.	I.	II.	III.	IV.
	cbc.		cbc.			cbc.		cbc.	
1	1000	6·7	250	12·8	10	30	77·7	5	77·5
2	250	12·8	60	28·4	11	30	78·2	5	77·6
3	60	28·4	15	43·4	12	30	78·5	5	77·6
4	15	43·4	5	60·7	13	30	78·6	5	78·3
5	30	74·1	5	75·8	14	30	80·4	5	79·2
6	30	77·0	5	77·3	15	30	80·9	5	78·9
7	30	77·1	5	77·5	16	30	87·6	5	80·6
8	30	77·3	5	77·4	17	30	92·5	5	85·9
9	30	77·3	5	77·4	18	30	97·4	5	90·4

Distilled under a higher pressure, this aqueous acid undergoes a change of composition. Under a pressure of 1·83 metre of mercury, the residual liquid attains a constant composition of 83·2 per cent. of real acid, and boils unchanged at 134°·6 C. The numbers have the same signification as in the preceding table.

II.—Distillation of Aqueous Formic acid under pressures greater than that of the atmosphere. (1) Pressure = 1·83 metre of mercury.

No.	I.	II.	III.	IV.	No.	I.	II.	III.	IV.
	cbc.		cbc.			cbc.		cbc.	
1	30	77·5	5	83·2	5	30	83·0	5	83·2
2	30	81·2	5	81·6	6	30	83·1	5	83·2
3	30	81·7	5	82·3	7	30	83·8	5	83·3
4	30	82·4	5	82·7					

(2) Pressure = 1·35 metre of mercury.

No.	I.	II.	III.	IV.
1	30 cbc.	77·8	5 cbc.	78·4
2	30 —	79·2	5 —	79·5
3	30 —	79·5	5 —	80·0
4	30 —	80·3	5 —	79·9

The liquid containing 80 per cent. of real acid boiled under a pressure of 1·35 metre of mercury at the fixed temperature of 124°·1 C.

In order to determine the relation between the quantities of acid and water existing in the liquid which vaporizes at the ordinary atmospheric temperature without undergoing change of composition, dry air was passed through aqueous formic acid of various degrees of strength until the residual liquid did not alter its composition. The results of the experiment are found in the following table, in which column I. gives the percentage of real acid contained in the liquid before passage of dry air through it; column II. the time during which the air passed; column III. the temperature of the liquid during the experiment; column IV. the fraction of the original volume to which the liquid was ultimately reduced; and column V. the percentage of real acid contained in the residual liquid.

III.—Passage of dry air through Aqueous Formic acid at the ordinary atmospheric temperature.

No.	I.	II.	III.	IV.	V.
1	77·3	24 hours	14°—15°C	$\frac{1}{2}$	77·1
2	77·1	8 —	15°C	$\frac{1}{2}$	68·4
3	68·4	24 —	12°—16°C	$\frac{1}{8}$	61·2
4	61·0	8 —	12°—15°C	$\frac{3}{4}$	60·3
5	60·3	16 —	14°—15°C	$\frac{1}{2}$	60·4
6	58·9	24 —	14°—15°C	$\frac{1}{2}$	59·6
7	59·6	16 —	12°C	$\frac{1}{4}$	59·3

From the above experiments it is clear that formic acid possesses no hydrate of simple atomic constitution having a constant boiling point; but that any number of mixtures of formic acid and water can be made, each one of which, distilled under a given pressure, will undergo no change in composition, and, therefore, must boil at a fixed point. In this respect, then, the behaviour of formic acid is exactly similar to that of the aqueous acids previously examined.

2. *Acetic Acid.*

It is well known that weak acetic acid gives on distillation a more watery distillate and a stronger residual acid. It is likewise stated in most Handbooks* that the aqueous acid containing 77 per cent. of real acetic acid ($\mathrm{C}\!\!\!-_2\,\mathrm{H}_4\,\Theta_2$), having the maximum density, and containing one atom of acid to one of water ($\mathrm{H}_2\Theta$), can be distilled without undergoing change, and boils at the fixed temperature of 104°C. The following experiments show that this latter statement is incorrect, and that no aqueous acetic acid exists which boils unchanged at a fixed temperature. It will be seen that acetic acid and water, when mixed in any proportions whatever, can be separated by distillation, the residue ultimately consisting of glacial acid; so that, in this respect, acetic acid differs from all the aqueous acids previously examined.

The analysis of the aqueous acetic acids was made with standard soda: 1003 equivalents of thrice recrystallised glacial acid being required to give the neutral litmus reaction with 1000 equivalents of soda.

I.—Distillation of aqueous acetic acid under the ordinary atmospheric pressure.

(1) A litre of aqueous acid containing 32·5 per cent. of real acid was distilled, the successive distillates and the residue being analysed. Column I. gives the volume of the distillate; column II. the percentage of real acid which each distillate contained:

No.	I.	II.	No.	I.	II.
1	50 cbc.	21·9	8	100 cbc.	28·8
2	100 —	23·6	9	100 —	33·7
3	50 —	23·2	10	50 —	37·1
4	75 —	23·2	11	50 —	40·1
5	100 —	25·2	12	50 —	45·1
6	100 —	26·8	13	50 —	65·8
7	100 —	28·7			

The residue of 25 cbc. contained 80·3 per cent. of real acid.

(2) 180 cbc. of a liquid containing 80·7 per cent. of real acid was distilled; three successive distillates contained 73·1, 81·0, and 89·3 per cent. of acid respectively; the residue of 20 cbc. contained 96·1 per cent of acid.

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* See Handwörterbuch der Chemie, article "Essigsaüre;" also Kekulé "Lehrbuch der Organischen Chemie," p. 563.

(3) 270 cbc. of a liquid containing 81·4 per cent. of real acid was distilled; five successive distillates contained 71·8, 74·4, 77·4, 81·6, and 85·2 per cent. of real acid respectively; the residue of 20 cbc. contained 97·9 per cent. of acid, and solidified on cooling.

(4) 50 cbc. of a liquid containing 77·5 per cent. of acid began to boil at 103°C. (Barom. = 760 m.m.); on distilling to $\frac{1}{6}$ of the original volume the boiling point rose to 113°C., and the residue contained 95·6 per cent. of acid.

(5) 50 cbc. of a liquid containing 79·0 per cent. of acid began to boil at 103°·3 C.; on distilling to $\frac{1}{6}$ the temperature rose to 112°C., and the residue contained 96·3 per cent. of acid.

(6) 50 cbc. of a liquid containing 80·0 per cent. of acid began to boil at 104°C.; on distilling to $\frac{1}{6}$ the temperature rose to 114°C., and the residue contained 96·8 per cent. of acid.

(7) 250 cbc. of a liquid containing 88·2 per cent. of acid on distillation to 15 cbc. left a residue which solidified on cooling, and contained 98·6 per cent. of real acid.

(8) 50 cbc. of a liquid containing 96·7 per cent. of acid, on distillation to 15 cbc. left a residue which solidified on cooling, and contained 98·8 per cent. of real acid.

(9) 50 cbc. of a liquid containing 91·7 per cent. of acid, on distillation to 15 cbc. left a residue which solidified on cooling, and contained 99·6 per cent. of real acid.

From these determinations it is seen, that aqueous acetic acid, distilled under the ordinary atmospheric pressure, splits up into water and glacial acid. The same result was obtained by distilling under pressures both greater and less than that of the atmosphere, as the following numbers show:—

II.—Distillation of aqueous acetic acid under pressures greater than that of the atmosphere:

Pressure = 1·310 metre of mercury.

(1) 60 cbc. of a liquid containing 81·4 per cent. of acid, on distillation to 15 cbc. left a residue containing 95·3 per cent. of acid.

(2) 60 cbc. of a liquid containing 90·7 per cent. of acid, on distillation to 10 cbc. yielded a residue which solidified on cooling, and contained 99·3 per cent. of acid.

III.—Distillation of aqueous acetic acid under pressure less than that of the atmosphere.

Pressure = 40 mm. of mercury.

(1) 50 cbc. of liquid containing 81·4 per cent. of acid, on distillation yielded a residue of 5 cbc. containing 92·5 per cent. of real acid.
(2) 50 cbc. of liquid, containing 89·7 per cent. of acid, on distillation gave a residue of 5 cbc. containing 95·1 per cent. of acid.
(3) 50 cbc. of liquid, containing 95·8 per cent. of acid, on distillation gave a residue of 5 cbc. which solidified on cooling, and contained 99·4 per cent. of acid.

The following determinations of the specific gravity of different aqueous acetic acids near the relation $\mathrm{C_2H_4O_2}$ to $\mathrm{H_2O}$, closely agree with Van Toorn's results*, and show that the aqueous acids containing from 76·5 to 80·0 per cent. of real acid possess the same specific gravity, so that no point of maximum density exactly corresponding to the compound of one of water to one of acid exists.

Per cent. of real acid.	Specific gravity at 15°·5 C.
76·5	1·0751 1·0753
77·5	1·0754 1·0754
79·0	1·0754
80	1·0754
98·5	1·0597
100·0	1·0563 1·0565

I beg to thank Mr. Schorlemmer for the aid which he gave me in carrying out the above experiments.

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* J. pr. Chem., 6, 171.

XXXVII.—*On Sombrerite.*

By Dr. T. L. Phipson, F.C.S.,
Member of the Chemical Society of Paris, &c., &c.

This mineral forms a large portion of some small islands in the West Indies, especially of Sombrero Island (N. lat. 18° 35′, W. long. 63° 28′), about 60 miles from St. Thomas. Its composition and properties prove it to be a new species, to which I have given the name sombrerite. It is remarkable for the large proportion of phosphoric acid it contains.

Sombrerite presents itself in nature as a white, yellowish white, or reddish coloured rock, having a straight fracture and, in some portions, a peculiar horny aspect; its appearance is, in general, compact, though, in reality, the rock is very porous. It shows no signs of crystallisation whatever, but appears like an amorphous, gelatinous phosphate that has been submitted to a high temperature. It is thought to be of comparatively recent geological origin, as it encloses fossil bones (of mammalia?) and several kinds of shells. In a mineralogical point of view, sombrerite is a compound of phosphate of lime with phosphate of alumina; in some specimens a portion of the alumina is replaced by a corresponding proportion of sesquioxide of iron; in others, where little or no iron is present, the mineral adheres to the tongue like other aluminiferous minerals. Sombrerite is not phosphorescent by heat like apatite; before the blowpipe, when moistened with sulphuric acid, it colours the flame pale green. It contains no fluoride or chloride of calcium.

The specific gravity of sombrerite is 2·52. A well-chosen specimen has given me the following composition:—

		Atomic ratio.	
Water	9·00	1·00	20
Phosphate of lime $\dot{\mathrm{C}}\mathrm{a}^3\overset{\cdot\,\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{P}}}$ ..	65·00	0·41	8
Phosphate of alumina $\overset{\cdot\cdot\cdot}{\cancel{\mathrm{Al}}}{}^2\overset{\cdot\,\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{P}}}{}^3$ ..	17·00	0·05	1
Carbonate of lime	5·00		
Chloride of sodium	1·44		
Sulphate of lime	1·36		
Silica	1·00		
Crenate of ammonia, &c. ..	0·20		
	100·00		

The formula of sombrerite is therefore $8\dot{\mathrm{C}}\mathrm{a}^3\overset{\cdot\,\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{P}}}+\overset{\cdot\cdot\cdot}{\cancel{\mathrm{Al}}}{}^2\overset{\cdot\,\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{P}}}{}^3+20\dot{\mathrm{H}}$

Persons who have seen this rock think that it owes its origin to guano, some looking upon it as "fossil guano," and others as "guano modified by volcanic action." In order to bring forward, if possible, some proof of these theories, I took a large quantity of the mineral and sought carefully for uric acid. Though the experiment was repeated several times, I have not been able to find the least trace of that compound, but only a very small quantity of *crenate of ammonia,* which I have frequently met with in many other minerals, notably in iron ores of various ages. At the same time it is possible that sombrerite may have derived its origin from ancient deposits of guano, modified by time and geological phenomena, as we see large beds of limestone and sandstone almost completely formed by the *débris* of organised beings. However that may be, I look upon this rock as having found its way to the surface at a high temperature, in contact with water or steam, and under great pressure. This would account for its peculiar appearance.

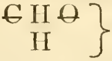
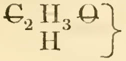
As regards the uses of sombrerite, I believe it has been employed already for the preparation of phosphorus, phosphoric acid, &c. But for agricultural purposes, though doubtless valuable, it presents a drawback to the manufacturer of "super-phosphate of lime." In producing the latter, sombrerite gives rise to a certain quantity of sulphate of alumina, and this salt being deliquescent, attracts and retains so much moisture that the product can be dried only with great difficulty.

Sombrerite has, however, the advantage of being easily reduced to powder, and could, in that state, be advantageously mixed with certain soils.

XXXVIII.—*Note on the Sulphur-compound formed by the action of Sulphuretted Hydrogen on Formate of Lead at a high temperature.*

By W. J. Hurst,

Student in the Laboratory of Owens College, Manchester.

In the year 1856, Limpricht* published an account of some analyses of a crystalline body, obtained together with formic acid by acting upon formate of lead heated to 200°—300°C with a current of sulphuretted hydrogen. As the result of his sulphur determinations he assigns to this body the formula  $\left.\begin{matrix}\cancel{C}\,\mathrm{H}\,\cancel{O}\\ \mathrm{H}\end{matrix}\right\}\cancel{S}$, naming it thioformic acid, and supposing it to be analogous to the thiacetic acid  $\left.\begin{matrix}\cancel{C}_2\,\mathrm{H}_3\,\cancel{O}\\ \mathrm{H}\end{matrix}\right\}\cancel{S}$ of Kekulé.*

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* Ann. Ch. Pharm., xcvii. 361.

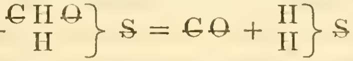
Seeing that the character of this interesting body has been but slightly investigated, I undertook, at the suggestion of Professor Roscoe, a further examination of its properties and the mode of its formation, the results of which, although mainly negative, I think it may be well to place on record.

When dry formic acid is acted on by pentasulphide of phosphorus, no trace of a sulphur acid is produced; the mixture distilled upwards continuously for several hours, slowly evolving sulphuretted hydrogen, the whole distillate boiling exactly at 101°C, and containing no sulphur in combination.

Heated in closed tubes to 106°C, the mixture underwent decomposition, but no thioformic acid was produced. So, likewise, when formic acid and pentasulphide of phosphorus were heated together under a total pressure of 3 atmospheres, torrents of sulphuretted hydrogen and carbonic oxide gases escaped, and the residual liquid all distilled over at 101°C, and contained no sulphur.

Formate of lead and pentasulphide of phosphorus distilled together, both in the dry and moist state, also yielded no thioformic acid.

From these experiments it is evident that thioformic acid cannot be produced by the method which Kekulé employed for the preparation of thiacetic acid. The elimination of sulphuretted hydrogen and carbonic oxide seems to point to a decomposition of the thioformic acid at the temperature of the experiments:

Thus— 

$$\left.\begin{matrix}\cancel{C}\,\mathrm{H}\,\cancel{O}\\ \mathrm{H}\end{matrix}\right\}\cancel{S} = \cancel{C}\cancel{O} + \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\cancel{S}$$

By Limpricht's method of decomposing formate of lead at a high temperature with a current of sulphuretted hydrogen, a solid crystalline body was obtained; but it was produced in much smaller quantities than Limpricht states; 15 kilos. of formate yielding only about 3 grammes of the purified substance.

The body, which crystallizes in beautiful long white needles, was purified by repeated crystallizations from hot formic acid, and dried completely in vacuo over sulphuric acid. The combustion of the substance was effected with chromate of lead in a long tube, the anterior part of which was not heated above low redness, according to the method lately described by Carius*, so that no peroxide of lead was required; and the water in the chloride-of-calcium-tube was found to be quite free from sulphurous acid. The sulphur was determined by oxidation with warm nitric acid; the sulphate of barium, being carefully rewashed with hydrochloric acid, and reweighed after incineration, to remove traces of nitrate of barium carried down.

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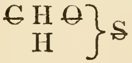
* Ann. Ch. Pharm., xc, 309. Phil. Mag., [4] vii, 518.

The results were as follows—

Calculated for the formula



$$\left.\begin{matrix}\cancel{\mathrm{C}}\,\mathrm{H}\,\cancel{\mathrm{O}} \\ \mathrm{H}\end{matrix}\right\}\cancel{\mathrm{S}}$$

Calculated		Found. (I.)	(II.)	(III.)	(IV.)
Carbon	19·3	27·93	29·25	28·21	
Hydrogen	3·2	4·70	4·83	5·23	
Sulphur	51·6	58·11	52·87	56·7	55·15
Oxygen	25·9				
	100·0				

Limpricht's numbers were—

Carbon	26·1	25·7	23·4
Hydrogen	5·6	4·7	6·3
Sulphur	51·2	52·5	
Oxygen			

From the foregoing analyses no definite formula can be deduced, in the absence of a vapour-density or accurate atomic weight determination, which the small quantity of the substance at my disposal unfortunately did not allow me to make. The analyses, however, show clearly that the body cannot be thioformic acid, as supposed by Limpricht, the excess of carbon over the theoretical quantity being too large to be explained by experimental error.

The purified substance, which showed under the microscope no trace of foreign bodies, but a perfectly homogeneous structure, crystallizes in white shining needles from solution in alcohol, ether, and acetic or formic acids, the alcoholic solution being neutral to litmus paper. The crystals melt at 120°C., and sublime unchanged at higher temperatures, depositing in long silky needles. The dry substance has a very slight odour, but its solution in formic acid has a strong penetrating sulphur smell.

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* Ann. Ch. Pharm., cxvi, 1.

It is not acted on either by hot or cold hydrochloric acid, but is easily decomposed by nitric and sulphuric acids; it is also unacted on by solutions of carbonate or hydrate of potassium, and by sulphide of ammonium. The alcoholic solution gives no precipitate with chloride of barium, but with nitrate of silver a heavy white precipitate soluble in ammonia and boiling alcohol, is produced. I did not succeed in obtaining from this silver-salt any atomic weight from which a satisfactory formula for the body could be calculated.

XXXIX.—*On the Capacity of Arsenious Acid for Bases, and on certain Arsenites.*

By Charles L. Bloxam.

In the *Journal of the Chemical Society*, vol. xii, p. 177, and vol. xiv, p. 143, I have recorded some experiments which tend to prove that boracic and silicic acids are respectively tribasic and bibasic; but that, in consequence of their feeble acid character, at moderately elevated temperatures, their capacity for bases becomes fully manifested, only when these are presented to them either in the uncombined state, or in some form of combination in which they are held by very feeble ties.

The object proposed in the commencement of the experiments which I now submit to the Society, was to ascertain whether similar results would be obtained with another feeble acid, the arsenious, the capacity of which for bases did not appear to have yet been satisfactorily determined.

Starting from the same point as in the experiments upon boracic acid, I first examined the action of arsenious acid upon the alkaline carbonates at different temperatures.

Action of Arsenious Acid upon the Carbonates of Potassa and Soda at 212°F.

A quantitative examination of the substances employed having proved their purity, two sets of experiments were made with each carbonate, in one of which, the acid, and in the other, the carbonate, was employed in excess.

When the arsenious acid was employed in excess, the experiment was conducted in the following manner. A weighed quantity of the alkaline carbonate was dissolved in water, the solution heated to 212°, and weighed quantities of arsenious acid added until the liquid refused to dissolve any more, even after long digestion*. It was then allowed to stand as long as any arsenious acid crystallised out, the clear liquid was evaporated to dryness on a water-bath, the residue dissolved in a very small quantity of water, and any undissolved arsenious acid (which was never in large quantity) added to that previously collected, and weighed after being dried at 212°†. By deducting the weight of this residual arsenious acid from that originally employed, the amount of acid which had combined with the alkali was ascertained. The alkaline arsenite was examined to prove that no carbonic acid had been retained, and that no arseniate of any consequence had been formed. The experiments were varied by using the opaque acid of commerce as well as that crystallised from hydrochloric acid, without affecting the results.

In those experiments in which the alkaline carbonate was employed in excess, the solution was evaporated to dryness on a water-bath, the residue dried at 212° until its weight was constant or nearly so, and the carbonic acid which it retained was determined in Fresenius and Will's apparatus. By deducting the weight of this carbonic acid from that known to be present in the alkaline carbonate employed, the amount of carbonic acid expelled by a given weight of arsenious acid was determined.

In stating the results, the equivalent of arsenious acid has been taken as = 99, that of carbonic acid = 22, of potassa = 47, and of soda = 31.

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* Solutions of the alkaline arsenites dissolve free arsenious acid much more rapidly than water, and arsenite of potassa is superior in this respect to arsenite of soda.

† It had been determined by a preliminary experiment that the loss experienced by arsenious acid, when repeatedly moistened and dried at 212°, would have no influence on the result.

Action of Arsenious Acid in excess upon Carbonate of Potassa at 212°F.

One equivalent (69) of carbonate of potassa employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
1	10·00	1·94
2	9·50	2·00

The excess of arsenious acid left undissolved by carbonate of potassa appeared, when examined by the microscope, in right rhombic prisms, and similar crystals of arsenious acid were sometimes deposited as the alkaline solution cooled, though the crystals then obtained were more frequently octohedral*.

The solution of arsenite of potash, obtained in these experiments, slowly deposited beautiful rectangular prisms having the composition $KO.HO.2AsO_3 + Aq.$†, and losing one equivalent of water at 212°F. (Experiment gave 3·26 instead of 3·42 per cent. of water expelled at 212°.)

The salt was analysed by acidulating its solution with hydrochloric acid, precipitating the arsenic by hydrosulphuric acid, and evaporating the filtered solution to obtain the chloride of potassium.

The arsenite dried at 212° in a current of dry air gave the following results.

	Found.	Calculated.
KO	19·09	18·51
$2AsO_3$	77·35	77·95
HO	3·53	3·54
	99·97	100·00

In order to determine the constitutional water, the salt was gently heated over a spirit-lamp in a glass tube through which a current of dry air was passed, the water being collected in a weighed tube containing chloride of calcium. The salt fused, with separation of traces of metallic arsenic and arseniuretted hydrogen, into a clear yellow liquid, which solidified on cooling to a very brilliant yellowish glass, extremely brittle and deliquescent*.

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* The separation of prismatic crystals of arsenious acid from a solution in potash has been mentioned by Pasteur.

† The same salt was obtained by Pasteur, who saturated potash with arsenious acid, and added alcohol.

The analysis of this *vitreous arsenite of potash* established for it the formula $KO.2AsO_3$.

	Found.	Calculated.
KO	19·44	19·18
$2\,AsO_3$	79·76	80·82
	99·20	100·00

A little arsenic acid was found in the vitreous mass even when the fusion was effected in a stream of carbonic acid.

As a control for the above analysis of this salt, 67·46 grns. of the crystallised bi-arsenite ($KO.HO.2AsO_3+Aq.$) were fused in a stream of dry carbonic acid, the water collected in a weighed tube containing chloride of calcium, and the gas then passed through bulbs filled with nitrate of silver to retain any arseniuretted hydrogen, of which a very slight trace only was detected. The water condensed in the drying-tube amounted to 4·57 grns. or 6·77 per cent. The loss suffered by the arsenite was 4·54 grns. The above formula for the crystallised salt requires a loss of 6·84 per cent. of water, exceeding by only 0·07 per cent. that found by experiment.

The vitreous arsenite of potash was also obtained (see exps. 16 and 17 in the Tables) by fusing carbonate of potash with an excess of arsenious acid.

Water dissolves the vitreous arsenite very readily, the solution gradually depositing crystals of the hydrated salt.

Strongly heated in a porcelain crucible, it emits copious vapours of metallic arsenic, and leaves an opaque mass of arseniate of potash.

The fused salt attacks platinum very readily, scraps of that metal being fused instantly when thrown into it, yielding a button of arsenide of platinum resembling grey cast-iron in character†. The abstraction of arsenic by the platinum had converted the arsenite into arseniate of potash. A little of the vitreous arsenite was heated in a hard glass tube to the softening point of the glass, without change, but on adding a few scraps of platinum, the salt was immediately converted into the arseniate.*

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* In the act of solidifying, this glass not only itself broke into several fragments, which were often projected with great force, but tore asunder any glass tube which contained it.

† The fused salt of the formula $KO.AsO_3$ had a similar effect upon platinum. 37·7 grains of this salt very easily effected the fusion of 42 8 grains of platinum at a red heat, the platinum having combined with 3·27 grns. of arsenic.

Action of Arsenious Acid upon an excess of Carbonate of Potassa at 212°F.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of potassa employed. Eqs.	Carbonic acid expelled. Eqs.
3	1·00	0·75
4	1·00	0·82
5	1·00	0·74
6	0·86	0·64
7	0·66	0·66

It appears, therefore, that when carbonate of potassa is acted on by an excess of arsenious acid at 212°, one equivalent of potassa combines with two equivalents of the acid, and that, if the carbonate is in excess, one equivalent of arsenious acid combines with two-thirds of an equivalent of potassa.

On evaporating the solution, in this last case, to a small bulk, it deposited crystals of the acid arsenite ($KO.HO.2AsO_3+Aq.$), but, by evaporating to dryness at 212°, a mass of prismatic crystals was obtained, having the composition $2KO.3AsO_3+3HO$, which did not lose water by protracted exposure in the water-oven. The analysis of this salt gave the following numbers:—

	Found.	Calculated.
$2KO$	21·76	22·48
$3AsO_3$	72·04	71·05
$3HO$	6·35	6·47
	100·15	100·00

When moderately heated, the salt fused to a transparent vitreous mass.

Action of Arsenious Acid in excess upon Carbonate of Soda at 212°F.

One equivalent (53) of carbonate of soda employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
8	4·09	1·91
9	4·20	1·93
10	5·90	1·95

---

* Gehlen noticed that arsenious acid heated with platinum and carbonate of soda gives arsenide of platinum and arseniate of soda.

Action of Arsenious Acid upon an excess of Carbonate of Soda at 212°F.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of soda employed. Eqs.	Carbonic acid expelled. Eqs.
11	2·00	0·69
12	1·00	0·67
13	1·00	0·69
14	1·00	0 66
15	0·66	0·66

The action of arsenious acid upon carbonate of soda at 212°F. is similar, therefore, to its action upon carbonate of potassa.

Neither of the solutions of arsenite of soda could be made to crystallise even after a great lapse of time. When the solution obtained with carbonate of soda and excess of arsenious acid was evaporated to dryness, and the residue dried at 212°, till of constant weight, it had the composition $NaO.2AsO_3$.

The solution of 3 eqs. of arsenious acid in 2 eqs. of carbonate of soda, when evaporated to a syrup on the water-bath, became black and assumed a peculiar metallic aspect, apparently from the separation of a minute quantity of finely divided metallic arsenic; it was kept for two months in this state, in an open basin, without change, but when diluted with water, after a short time it became colourless. Since long exposure *in vacuo* over sulphuric acid did not induce crystallisation, it was dried up, with great difficulty, on the water-bath, when it left a grey mass of confused prismatic crystals. After being dried at 212° till its weight became constant*, it was analysed with the following results:—

	Found.	Calculated.
$2NaO$	16·57	17·27
$3AsO_3$	83·40	82·73
	99·97	100·00

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* During the drying of the alkaline arsenites, a faint alliaceous odour was generally observed, and nitrate of silver exposed on paper above the capsules became slightly blackened, indicating the evolution of a little arseniuretted hydrogen, produced by the decomposition of water, and attended with the formation of arsenic acid, traces of which were always discovered in the dry salts. A point was usually arrived at when the drying mass had assumed the consistence of honey, which it would retain even after long heating, until briskly stirred, when it became a very hard solid mass.

The salt was found to contain a very little arsenic acid, as might be expected from the separation of metallic arsenic mentioned above, arising probably from the splitting of a part of the arsenious acid ($5AsO_3 = 3AsO_5 + As_2$). The circumstance that so little arsenic acid was present is worth notice, since the syrupy arsenite had been exposed to the air for at least two months in a capsule covered with filter paper.

Action of Arsenious Acid upon the Carbonates of Potassa and Soda at a low red heat.

For these experiments, the heat of an Argand gas-burner was employed. Weighed quantities of arsenious acid and the alkaline carbonate were dissolved in water, in a porcelain crucible, the solution gently evaporated to dryness, and the residue gradually heated till its weight was constant. When an excess of arsenious acid was employed, the amount retained in combination by the alkali was ascertained by deducting the known weight of the latter from the total weight of the residue, previously tested for carbonic and arsenic acids. When the alkaline carbonate was in excess, the amount of carbonic acid expelled was inferred by deducting the weight of the residue, previously tested for arsenic acid, from the joint weights of the alkaline carbonate and arsenious acid, care being taken that the latter had not been volatilised during the experiment.

Action of Arsenious Acid in excess upon Carbonate of Potassa at a low red heat.

One equivalent (69) of carbonate of potassa employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
16	2·50	1·95
17	2·50	2·02

The product was a transparent glassy mass of $KO.2AsO_3$, having a dark colour, caused by the separation of a little arsenic in the metallic state.

Action of Arsenious Acid upon an excess of Carbonate of Potassa at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of potassa employed. Eqs.	Carbonic acid expelled. Eqs.
18	1·00	1·09
19	1·00	1·05
20	1·00	1·04
21	1·25	1·06

It is evident, from these results, that an excess of arsenious acid acts upon carbonate of potassa, at a red heat, exactly as at 212°, but that the acid is capable of combining with one equivalent of potassa when heated to low redness with an excess of the carbonate.

Action of Arsenious Acid in excess upon Carbonate of Soda at a low red heat.

One equivalent (53) of carbonate of soda employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
22	2·5	1·97

The result of this experiment was a transparent vitreous mass of $NaO.2AsO_3$.

Action of Arsenious Acid upon an excess of Carbonate of Soda at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of soda employed. Eqs.	Carbonic acid expelled. Eqs.
23	1·50	1·04

It appears, therefore, that, contrary to the expectations which I had been led to form by the behaviour of boracic and silicic acids, arsenious acid acts upon carbonate of soda in precisely the same manner as upon carbonate of potassa, both at 212°, and at a low red heat, and that the capacity of arsenious acid for bases of the formula MO, as measured by its action upon the alkaline carbonates, does not extend beyond one equivalent.

Action of Arsenious Acid upon the Hydrates of Potassa and Soda.

The experiments under this head were made in the same manner as those upon boracic and silicic acids described in the Society's Journal for July, 1861 (p. 143), the hydrates being fused in a silver tray, heated in a current of pure and dry air, until of constant weight, a known quantity of arsenious acid introduced, enough water added to nearly fill the tray, the whole then slowly evaporated to dryness in the current of air, and afterwards moderately heated over an Argand gas burner until no material loss of weight was perceptible.*

Action of Arsenious Acid upon Hydrate of Potassa at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Hydrate of Potassa employed. Eqs.	Water (HO = 9) expelled. Eqs.
24	4·10	1·45
25	4·50	1·58
26	2·20	1·32

Action of Arsenious Acid upon Hydrate of Soda at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Hydrate of Soda employed. Eqs.	Water expelled. Eqs.
27	3·00	2·29
28	10·00	2·29
29	17·00	2·14
30	8·60	2·04

On examining the products of these experiments, a considerable quantity of arsenic acid was always detected, even when hydrogen, nitrogen, or coal-gas had been employed instead of atmospheric air, and it was proved by direct experiment, in an atmosphere of nitrogen, that when arsenious acid or an alkaline arsenite is fused with an excess of alkaline hydrate, an arseniate is formed, at the expense of the oxygen of the water, the hydrogen of which is disengaged, unaccompanied by arseniuretted hydrogen.

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* It had been determined, by a preliminary experiment, that the hydrates suffered no alteration in weight when dissolved in water and evaporated in this manner.

When a small excess of the alkaline hydrate was employed, one portion of the arsenious acid was oxidised at the expense of the remainder, metallic arsenic being disengaged.

Although, on account of these decompositions, no reliance can be placed upon this method for the determination of the capacity of arsenious acid for bases, it is interesting to observe that (as was found in the cases of boracic and silicic acids) the hydrate of soda is decomposed by arsenious acid to a greater extent than hydrate of potassa.

Having failed hitherto to obtain any conclusive evidence as to the capacity of arsenious acid for bases, I next proceeded to determine the composition of such of the arsenites as appeared most likely to aid in solving the question.

Arsenite of Silver.

The formula of the yellow arsenite of silver has been given by Pasteur as $2AgO.AsO_3$ and by Filhol as $3AgO.AsO_3$.

Believing that the discrepancy was caused by the tendency of the precipitate to carry down adhering arsenious acid, I dissolved a weighed amount of pure bi-arsenite of potash ($KO.HO.2AsO_3$) in so much water that no arsenious acid was separated when a portion of the solution was acidulated with nitric acid and set aside. A measured quantity of the alkaline solution was then tested with a standard solution of nitrate of silver, added as long as any precipitate was produced. Each equivalent of the arsenite was found to require 1·5 eqs. of nitrate of silver.

The yellow precipitate, which was at first very bulky, but became crystalline on standing, and strongly adherent to the lines made by the stirring-rod, was washed and dried at 212°. It appeared in tufts of needles under the microscope.

For the analysis of this precipitate, it was oxidised by nitric acid, the silver precipitated by hydro-chloric acid, and the arsenic acid in the filtrate determined as arseniate of magnesia and ammonia. The results were—

Oxide of silver*	74·77 per cent.
Arsenious acid	25·88 ,,

Since the formula $2AgO.AsO_3$ would require only 70·9 per cent. of oxide of silver, and the liquid from which the precipitate had separated was decidedly acid, it appears highly probable that the precipitate was a mixture of $3AgO.AsO_3$ with an excess of arsenious acid.

The decomposition of the bi-arsenite of potassa by nitrate of silver would therefore be represented by the equation.

$$2(KO.HO.2AsO_3) + 3(AgO.NO_5) =$$
$$3AgO.AsO_3 + 2(KO.NO_5) + HO.NO_5 + 3AsO_3 + HO.$$

The filtrate from this precipitate was mixed with more nitrate of silver, and carefully neutralised with ammonia. A fresh precipitate, similar to the preceding, was obtained. Dried at 212°F., it was found to contain 22·19 per cent. of arsenious acid, the formula $3\ AgO.AsO_3$ requiring 22·15.

The sesquiarsenite of soda $(2NaO.3AsO_3)$ was found to require 2 eqs. of nitrate of silver for complete precipitation, yielding a precipitate of $3\ AgO.AsO_3$, and a very feebly acid solution.

$$3(2NaO.3AsO_3) + 6(AgO.NO_5) =$$
$$2(3AgO.AsO_3) + 7AsO_3 + 6(NaO.NO_5).$$

Arsenites of Lead.

Two arsenites of lead were analysed by Berzelius, viz., $PbO.AsO_3$ obtained by saturating ammonia with arsenious acid, and precipitating by neutral acetate of lead, and $2PbO\ AsO_3$ prepared in a similar manner with tribasic acetate of lead. I dissolved one equivalent of acetate of lead in water, mixed the solution with ammonia in excess, and added it to an aqueous solution of half an equivalent of arsenious acid.

The precipitate was well washed, dried at 212°, and analysed by oxidising it with nitric acid, precipitating the lead as sulphate, and the arsenic as arseniate of magnesia and ammonia.

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* Ag=108.

	Found.	Calculated.
2PbO*	68·39	69·28
AsO_3	31·43	30·72
	99·82	100·00

Another arsenite of lead was prepared by precipitating a dilute solution of bi-arsenite of potassa (I) or of sesquiarsenite of soda (II) by nitrate of lead.

The precipitates, dried at 212° till of constant weight, gave the following results on analysis.

	Found.		Calculated.
	I.	II.	
3PbO	60·81	60·72	59·80
$2AsO_3$	34·70	34·45	35·36
3HO (by difference)	4·49	4·83	4·84
	100·00	100·00	100·00

I am disposed to believe that this salt $3PbO.3HO.2AsO_3$ is formed upon the tribasic type 2 ($3MO.AsO_3$), having three atoms of water in the place of fixed base.

Arsenite of Copper.

The precipitates of arsenite of copper were analysed by oxidising them with nitric acid, precipitating the arsenic acid as arseniate of magnesia and ammonia, acidulating the filtrate with hydrochloric acid, and precipitating the copper either by hydrosulphuric acid or by hyposulphite of soda. The result was controlled by determining the arsenious acid volumetrically with a standard solution of permanganate of potash.

By mixing a dilute solution of the biarsenite of potash ($KO.HO.2AsO_3$) with sulphate of copper as long as any precipitate was formed, a decidedly acid filtrate was obtained, and the precipitate, when dried at 212°, was found to contain

Oxide of copper†	1·88 eqs.
Arsenious acid	1·00 „
Water	1·16 „

---

* Pb = 103·6.

† Cu = 31·7.

The composition of this precipitate rendered it probable that, like the arsenite of silver, it had carried down an excess of arsenious acid, and that its true formula should be $2\,CuO.HO.AsO_3$.

On adding more sulphate of copper to the liquid filtered from this precipitate, and carefully neutralising with ammonia, a further precipitate was obtained, which was found, after drying at 212°, to contain

Oxide of copper	.. 2·21 eqs.
Arsenious acid.. ..	.. 1·00 ,,
Water	.. 1·26 ,,

so that it was probably the same salt ($2\,CuO.HO.AsO_3$) which had now carried down an excess of hydrated oxide of copper.

The precipitate obtained from sesquiarsenite of soda ($2NaO.3AsO_3$) and sulphate of copper, when dried at 212°, contained

Oxide of copper	.. 2·35 eqs.
Arsenious acid.. ..	.. 1·00 ,,
Water	.. 0·92* ,,

By mixing an aqueous solution of arsenious acid with ammonio-sulphate of copper, a precipitate was obtained which, when dried in air till of constant weight, contained

Oxide of copper ..	.. 2·02 eqs.
Arsenious acid ..	.. 1·00 ,,
Water	.. 2·89 ,,

After drying *in vacuo* over sulphuric acid, it gave

	Found.	Calculated.
$2CuO$	42·69	42·40
AsO_3	52·67	52·80
HO (by difference)	4·64	4·80
	100·00	100·00

Admitting the water to play the part of a base, the arsenite of copper is formed upon the tribasic type.

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* Scheele's prescription for the commercial green arsenite of copper involves 2·3 eqs. of oxide of copper for 1 eq. of arsenious acid, so that Scheele's green, dried at 212°, appears to be essentially a mixture of $2CuO.HO.AsO_3$ with an excess of oxide of copper.

Arsenite of Baryta.

When a solution of arsenious acid in ammonia was precipitated by chloride of barium, a gelatinous semi-transparent precipitate was obtained, which was dissolved to a very considerable extent by water (yielding an alkaline solution), was dried with great difficulty, and absorbed carbonic acid from the air, so that it was very unfit for accurate analysis.

However, it was dried at 212°, dissolved in hydrochloric acid, the baryta precipitated as sulphate, and the arsenious acid determined in the filtrate by precipitation with hydrosulphuric acid. It gave

Baryta*	1·00 eqs.
Arsenious acid	0·87 „
Water	1·93 „

Another specimen, prepared by decomposing a solution of sesquiarsenite of soda ($2NaO.3AsO_3$) with two equivalents of chloride of barium, gave, when dried at 212°,

Baryta	1·00 eqs.
Arsenious acid	1·21 „
Water	1·96 „

The salt prepared by this method would probably have carried down with it an excess of arsenious acid, whilst that first prepared had retained some carbonate of baryta.

I did not succeed in obtaining a more satisfactory specimen of this salt, but if it be allowable to take the mean of the above results

Baryta	1·00 eqs.
Arsenious acid	1·04 „
Water	1·94 „

the formula of the arsenite of baryta dried at 212°, would be $BaO.2HO.AsO_3$.

Arsenite of Magnesia.

A cold saturated solution of arsenious acid is not precipitated by sulphate of magnesia, but a mixture of this salt with chloride of ammonium and ammonia throws down a white pulverulent amorphous precipitate which does not contain ammonia.

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* Ba = 68·5.

A solution of 1 part of arsenious acid in 150 parts of water gave an abundant precipitate with the ammoniacal magnesia solution, on stirring, and even when 700 parts of water were present, the precipitate was obtained after a few minutes, which renders it necessary to be cautious in the employment of the magnesia test for arsenic and phosphoric acids when arsenious acid is present in the liquid.

In order to determine the composition of the arsenite of magnesia, it was dissolved in nitric acid, which oxidised it with great violence, even without the application of heat, and the solution mixed with chloride of ammonium and excess of ammonia, which precipitated the whole of the arsenic and magnesia as arseniate of magnesia and ammonia, from the weight of which those of the magnesia and arsenious acid were deduced. The water was determined directly by heating the salt in a current of dry air, and collecting the water in a tube filled with chloride of calcium.

The result of the analysis was confirmed by determining the arsenious acid with a standard solution of permanganate of potash.

Dried at 212° F.

	Found.	Calculated.
2MgO*	25·63	25·48
AsO_3	63·44	63·06
2HO	10·73	11·46
	99·80	100·00

Dried at 400° F.

	Found.	Calculated.
2MgO	26·93	27·03
AsO_3	66·66	66·89
HO†	5·07	6·08
	98·66	100·00

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* Mg=12.

† Had the water been determined by difference, it would have amounted to 6·41 per cent. It was, of course, difficult to determine the water exactly in such a salt at so high a temperature.

Dried above 400° F.

	Found.	Calculated.
2MgO	28·29	28·78
AsO_3	70·04	71·22
	98·33*	100·00

The composition of the arsenite of magnesia dried below 400° F. ($2MgO.HO.AsO_3$) also supports the tribasic character of arsenious acid.

Arsenite of Zinc.

This salt, which was the most remarkable and definite of the precipitated arsenites, was prepared in the following manner:

Solution of sulphate of zinc was mixed with ammonia till the greater part of the precipitate had re-dissolved; a considerable quantity of chloride of ammonium was then added, the solution filtered, and mixed with an excess of a cold saturated solution of arsenious acid. A white bulky precipitate was thus obtained, which shrank excessively on standing, and exhibited the character possessed by crystalline precipitates of adhering very strongly to the lines made by the stirring-rod. When examined under the microscope, however, it was found to consist of very beautiful semi-transparent globules, in most cases so perfectly spherical that it was difficult to prevent them from rolling about on the microscope-slide, where they had much the appearance of some farinaceous substance.

When dried at 212°, this arsenite of zinc became a glistening pearly powder. The analysis of this specimen precipitated from the strongly alkaline solution is given as I in the following Table.

The filtrate from this precipitate was partly neutralised with sulphuric acid, when a fresh precipitate of the same character was obtained, the analysis of which is given under II.

On further neutralising with sulphuric acid, opaque globules were obtained, which proved, on analysis, to contain an excess of arsenious acid.

The arsenite of zinc was analysed by dissolving it in hydrochloric acid, precipitating the arsenious acid by hydrosulphuric acid, evaporating the solution, and precipitating the oxide of zinc by carbonate of soda. The results were verified by determining the arsenious acid with permanganate of potash.

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* A little water was still retained.

Arsenite of Zinc dried at 212°.

	Found.			Calculated.
	Sp. I.	Sp. II.	Mean.	
3ZnO* ..	55·29	54·74	55·01	55·23
AsO_3 ..	44·55	44·99	44·77	44·77
	99·84	99·73	99·78	100·00

The composition of the arsenite of zinc, like that of the arsenite of silver, establishes the capacity of arsenious acid for three atoms of a base of the formula MO.

Arsenite of Ammonia.

A salt of the formula $NH_4O.AsO_3$ having been described by Pasteur and by De Luynes, I was anxious to ascertain whether, in the presence of a large excess of ammonia, a more highly basic salt could be obtained.

Arsenious acid dissolves with difficulty in strong ammonia, but if water be added, the solution is effected much more rapidly, and on afterwards adding more strong ammonia, a precipitation of minute prismatic crystals takes place. These crystals were rapidly washed with alcohol, and dried by violent pressure between blotting paper, since they deliquesced and evolved ammonia very rapidly in the air. For analysis, the salt was weighed out in hydrochloric acid, the arsenic precipitated as sulphide, and the chloride of ammonium in the filtrate determined by evaporation. A verification for the ammonia was obtained by an alkalimetrical determination, and for the arsenious acid by permanganate of potash. The analysis fully corroborated the remarkable formula $NH_4O.AsO_3$ assigned by De Luynes.

	Found.		Calculated.
	De Luynes.	C. L. B.	
NH_4O	22·07	20·48	20·80
AsO_3	77·93	79·09	79·20
	100·00	99·57	100·00

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* Zn = 32·7.

The existence of the following arsenites appears now to have been established.

Monobasic Arsenites.

$KO.AsO_3$	Pasteur	C. L. B.	
$NaO.AsO_3$	„	„	
$NH_4O.AsO_3$	„	„	De Luynes
$BaO.AsO_3$	Filhol		
$CaO.AsO_3$	Simon		

Bibasic Arsenites.

$2KO.AsO_3$	Pasteur	
$2NaO.AsO_3$	„	
$2BaO.AsO_3$	Filhol	
$2CaO.AsO_3$	Simon	
$2MgO.AsO_3$	C. L. B.	
$2PbO.AsO_3$	Berzelius	C. L. B.

Tribasic Arsenites.

$BaO.2HO.AsO_3$ (?)	C. L. B.	
$2MgO.HO.AsO_3$	„	
$2CaO.HO.AsO_3$	Simon	
$2CuO.HO.AsO_3$	C. L. B.	
$3PbO.3HO.2AsO_3$	„	
$3ZnO.AsO_3$	„	
$3AgO.AsO_3$	„	Filhol

Sesquiarsenites.

$2KO.3AsO_3+3Aq$	C. L. B.
$2NaO.3AsO_3$	„

Acid Arsenites.

$KO.HO.2AsO_3+Aq.$	Pasteur	C. L. B.
$KO.2AsO_3$		„
$NaO.2AsO_3+xAq.$	„	„
$NaO.2AsO_3$		„

Although the composition of these salts leaves some doubt as to whether arsenious acid should be regarded as tribasic, I am much inclined to that belief by the following considerations—

The normal sulpharsenites of potassium and ammonium have, according to Berzelius, the formulæ $3KS.AsS_3$ and $3NH_4S.AsS_3$.

Phosphorous acid (PO_3) which should present a very close analogy to arsenious acid, has a tribasic character: for its crystallised hydrate has the formula $3HO.PO_3$; and although the phosphites of soda, baryta, and lead, are represented by Wurtz as $2NaO.PHO_4$, $BaO.HO.PHO_4$ and $2PbO.PHO_4$, they might plausibly be written on the tribasic type, as $2NaO.HO.PO_3$, $BaO.2HO.PO_3$ and $2PbO.HO.PO_3$.*

Boracic and arsenious acids are interchangeable in the class of tartrates known as *emetics,* so that if the former be really a triatomic group, as represented in a former communication, it is probable that the latter is so.†

I have not yet completed the examination of the arsenious ether obtained by decomposing one equivalent of terchloride of arsenic with three equivalents of sodium-alcohol; but I have every reason to believe, that it contains three equivalents of oxide of ethyl to one of arsenious acid.

XL.—*Description of a combined Maximum and Minimum Mercurial Thermometer.*

By W. Symons.

In 1860 I exhibited at the Pharmaceutical Society a double registering mercurial thermometer which had acted perfectly for some time, but soon afterwards that and other similar tubes were deranged by the mercury separating, thus destroying the usefulness of the instrument. When showing the first instrument to Dr. Redwood, he informed me that Dr. Macvicar had described a somewhat similar instrument at the Chemical Society; but, on reference, I found that while he used two fluids, his tube was straight, so that to have an open scale the thermometer must be inconveniently long: my instrument had an advantage in this respect, as by doubling the tube it was rendered more portable.

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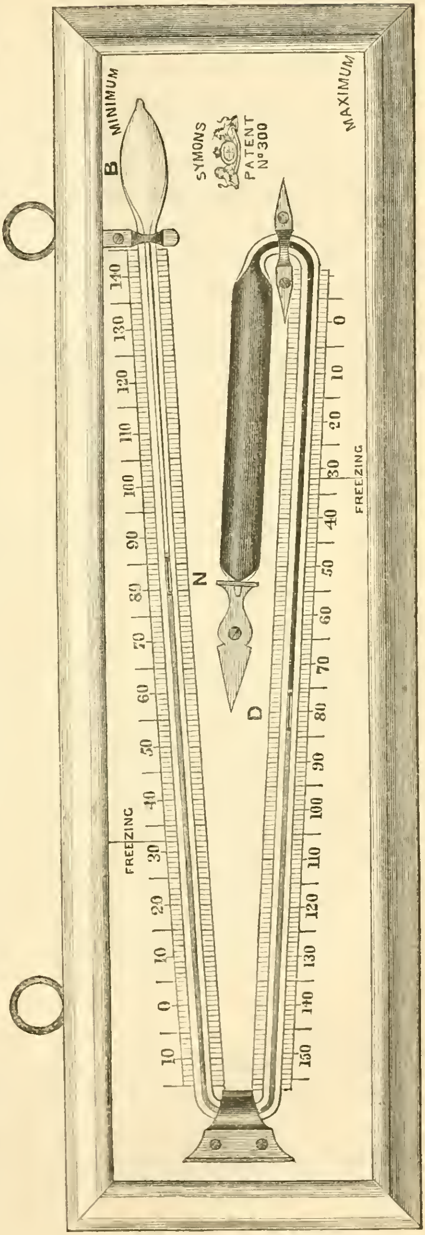
* Nitrous acid is commonly grouped with arsenious and phosphorous acids. Bromeis has described $3PbO.NO_3$ and $2PbO.NO_3 + HO$, whilst Pasteur has recently obtained $CuO.NH_4O.HO.NO_3$.

† It is worth notice that both boracic and arsenious acids form vitreous bi-acid salts with the alkalies.

From Dr. Macvicar's remarks (Journal of Chem. Soc., vol. xi, page 106) it is doubtful whether he had ever constructed a satisfactory instrument. He says,—"Between 20 and 30 years ago Mr. Adie, of Edinburgh, to prevent oxidation in Rutherford's maximum thermometer, introduced, above the mercury, naphtha; and I saw, the other day, one of these thermometers which, during that long interval, had preserved the mercurial column unbroken." Dr. Macvicar had no doubt tried some unsuccessful experiments in consequence, as he adds:—"It is certain, however, that it is not every kind of liquid that passes under the name of naphtha that will do so." My expeience would lead me to say, it is not any kind of such liquid that will do so. I have tried every such liquid that I could procure, and a variety of others kindly supplied to me by a Fellow of this Society, but without success.

After pursuing the subject for some time with alcohol, naphtha and various hydro-carbons, the thought suggested itself to me to experiment with a totally different class of liquids, selecting those with a high specific gravity. During the winter of 1860 and 1861 I had a variety of tubes exposed to all the frosts of that very severe season, and was happy to find some of these experiments much more successful. Sulphuric acid of various strengths, mixtures of sulphuric acid with sulphate of soda and alum, and a solution of common salt nearly saturated, stood the test without freezing and without the mercury being separated. Some of the original tubes are now shown, and also a thermometer with dilute sulphuric acid, made in January, 1861, it will be seen to have worked satisfactorily. Since that time, a great number have been made and sent successfully to all parts of the British Islands; but, bearing in mind the failure of my first attempt, I have waited until this arrangement has been fully and fairly tested before bringing it more distinctly before the scientific public.

As I have alluded to Dr. Macvicar's second instrument, I may be allowed perhaps to add that the first described by him in vol. x, p. 221, is very similar to a thermometer suggested long since by Dr. Traill, and described in the "Library of Useful Knowledge." In stating this, I would not for a moment insinuate that it was not an original idea of Dr. Macvicar's; for all who have the slightest knowledge of that gentleman will fully acquit him of appropriating to himself knowingly the suggestions of others; but it may be mentioned, as one amongst the many instances of the independent reproduction of similar inventions by different individuals.



The thermometer now shown consists of a tube bent as in the figure; the cylindrical bulb and tube up to D are filled with mercury, and from D to N with dilute acid; the upper bulb B and the tube to N are filled with air; at D and N are inserted steel indices covered with glass; the index D acts just as the index in Rutherford's maximum thermometer, and the index N as a minimum.

The advantages of this instrument, as compared with Rutherford's, are: 1st. That it combines the two instruments in one; 2nd. As the maximum index floats in a dense liquid, the thermometer is never deranged by the index sinking into the mercury; and, 3rd. It is virtually a mercurial minimum. The advantages over Six's form are: 1st. It is a mercurial thermometer; 2nd. The tubes being nearly horizontal, spring indices are not required; the tubes can, therefore, be smaller, and a frequent source of derangement, especially in carriage, is avoided; and, 3rd. The disadvantages and inaccuracies in extreme temperatures, either high or low, arising from the high specific gravity of mercury, does not exist in the new instrument.

The indices are set either with or without a magnet, as most convenient.

My friend and namesake, Mr. G. J. Symons, of Camden Town, who is probably known to many connected with this Society, as a meteorologist, kindly undertook to compare the daily readings of one of these instruments with two others of the usual kind, supplied by different makers of repute; and the result will, I think, show that this instrument may be depended on even for scientific observations, the average discrepancies being under two-tenths of a degree, and these may be accounted for, to some extent, at least, by the respective bulbs being not exactly in similar circumstances with regard to passing currents of air.

XLI.—*Additional Notes on Reciprocal Decomposition among Salts in Solution.*

By J. H. Gladstone, Ph.D., F.R.S.

Since the publication of my paper on "Circumstances modifying the action of Chemical Affinity,"[*] and of "Some experiments illustrative of the reciprocal Decomposition of Salts,"[†] I have from time to time thought and experimented further upon the subject. The present communication is simply a gathering together of such observations as appear to me capable of throwing additional light on these laws of combination.

I reserve to some future occasion the experiments I have made on the time required to bring about a perfect state of equilibrium among various salts in solution, as the results are not yet sufficiently matured for publication, and the subject is a very distinct one.

The ultimate disposition of the various elements in solution is independent of the manner in which they were originally combined.

Suppose there be two basic elements M and M′, and two salt-radicles R and R′; the question is, whether if MR′ be added to

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[*] Phil. Trans., 1855, 179.

[†] Chem. Soc., Qu. J. ix, 144.

M′R in solution, the same distribution of elements will take place as if MR were added to M′R′. From the law of reciprocal decomposition it follows, as something like a corollary, that it must be so, and in my first paper I was content with one quantitative experiment; yet, as the opposite has been contended for, I thought it well to test the law in other instances.

The former experiment was this:—Two solutions were prepared, the one containing equivalent proportions of sulphocyanide of potassium, sulphate of potassium, and ferric nitrate; the other, equivalent proportions of sulphocyanide of potassium, nitrate of potassium, and ferric sulphate. These two mixtures, each containing the same absolute quantity of salts, were made up to the same volume with water; and the resulting colour was found to be identical, leading to the inference that the ultimate distribution of the four salts in each solution was the same.

The law was tested with a mixture of single equivalents of acetate of copper and nitrate of lead, and a mixture of single equivalents of acetate of lead and nitrate of copper. The colour was identical. A similar result was also obtained with sulphate of copper and nitrate of potassium, as compared with nitrate of copper and sulphate of potassium.

But it would rarely happen that a result perceptible to the eye could be obtained in this manner. The majority of metals that give colour to their compounds produce (unlike iron and copper) the same or nearly the same tint with whatever radicle they may be combined; and the same holds good with the colour-producing acids; whilst the great multitude of salts are colourless, and therefore invisible in solution. It occurred to me, however, that perceptible reactions might be obtained with these also, if mixtures were made of two colourless salts and then added to some coloured salt, such as ferric sulphocyanide, which is capable of reduction in colour by a redistribution of its components. The amount of alteration in this third salt would, of course, depend on the proportion of all the four salts ready to act upon it; indeed, the question would just be enlarged so as to include six elements instead of four —M, M′, and M″ with R, R′, and R″.

The experiment was tried in this manner:—Equivalent quantities of the sulphate and nitrate of potassium, and the sulphate and nitrate of magnesium, were dissolved in equal volumes of water; a mixture was made of equal quantities of the solutions of sulphate of potassium and nitrate of magnesium, and another mixture of equal quantities of the solutions of sulphate of magnesium and nitrate of potassium: these were added to two equal portions of a solution of sulphocyanide of iron in the isoscope; and the diminution of the colour effected by them was observed. Now, the sulphate of potassium is known to have a much greater power of reducing the sulphocyanide than the nitrate has, but it was found that the two mixtures produced exactly the same tint.

In like manner, acetate of potassium with nitrate of lead produced the same diminution of colour (within the limits of probable errors of experiment) as acetate of lead and nitrate of potassium. The same two mixtures were tried also on ferric meconate, and gave a similar result.

The same experiment on the red sulphocyanide was also made with mixtures respectively of sulphate of copper with nitrate of of magnesium, and sulphate of magnesium with nitrate of copper. The same shade was produced by each.

A similar result was obtained with chloride of sodium mixed with sulphate of magnesium, and sulphate of sodium mixed with chloride of magnesium. These two mixtures were also tried on the deep scarlet bromide of gold, and they were found to produce an equal reduction of the colour. The two had the same effect likewise on a solution of the double iodide of platinum and potassium.

Two solutions were prepared, the one of the double sulphate of copper and potassium, the other of an equivalent of sulphate of potassium mixed with an equivalent of sulphate of copper. They produced the same effect on a solution of ferric sulphocyanide. This experiment is of importance, not because there was much doubt, *à priori*, that the condition of a double salt in solution is the same whether it has ever been crystallized or not, but because at first sight some experiments recorded by Professor Graham seem to point to the opposite conclusion. He found, in respect to the salt above mentioned, and the sulphate of magnesium and potassium, that the double salt was more diffusible than its mixed constituents.* Yet this seems to be the case only when the solutions are freshly prepared and in the cold, and the discrepancy probably arises solely from the slowness of the action by which uniformity is ultimately produced.

When there are several salts with the possibility of solid matter forming, the ultimate result may indeed be influenced by the order in which they are mixed. Thus, in the experiment above narrated, with chloride of sodium and sulphate of magnesium compared with chloride of magnesium and sulphate of sodium, it was only when the salts were mixed together beforehand that they equally reduced the iodide of platinum and potassium. When they were added one after the other to the red salt, a deposit of platinum separated in the one case, though not in the other. This, however, is not a real exception to the general rule, which only refers to salts actually in solution.

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* Phil. Trans., 1850, 22.

Extension of M. Margueritte's experiment.

M. Margueritte has shown,* by a number of instances, that if a salt MR is less soluble in water than another salt M'R', or than MR' or M'R, the addition of M'R' causes a larger quantity of it to be dissolved. One instance is that of chlorate of potassium, which is more soluble in a solution of chloride of sodium than in pure water. Now, from the law of reciprocal decomposition (of which this is a result), it was foreseen that after a single equivalent of the more soluble salt M'R' had exerted its influence, a second equivalent would produce an additional effect, though to a smaller extent, and so on. On trying the experiment, this was found to be the case. 129 grm. of chlorate of potassium and 59 grm. of chloride of sodium were taken as equivalent proportions.

Chlorate of Potassium.	Chloride of Sodium.	Water required for solution.	Decrease for each equiv. of Chlor. Sodium.
1 equiv.	0	2493 meas.	0
1 „	1 equiv.	2208 „	285 meas.
1 „	2 „	2060 „	148 „
1 „	4 „	1910 „	75 „

If a compound MR *is rendered more soluble by the presence of another compound* M'R', *the addition of either* MR' *or* M'R *will precipitate it from its saturated solution.*

This is also a necessary consequence of the law of reciprocal decomposition: for the MR' or M'R will produce more MR, and the liquid is incapable of holding any more of this compound in solution. In a former paper, I examined one particular case of this general law, namely, when a salt insoluble in water dissolves in an aqueous solution of an acid; and the law was found to hold good in every instance except one. That apparent exception was in the case of ferric phosphate dissolved in hydrochloric acid, from which a precipitate was not obtained by the addition of phosphoric acid; but I have since found that phosphate of iron, freshly prepared by double decomposition, and well washed, dissolves in phosphoric acid, and thus the anomaly is fully explained. I have lately observed another apparent exception in the case of phosphate of calcium dissolved in hydrochloric acid, and this admits of another explanation, for the tribasic phosphate dissolves in three equivalents of the acid; therefore, if on the addition of phosphoric acid, any chloride of calcium be decomposed, the hydrochloric acid set free will suffice to dissolve the phosphate of calcium produced.

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* Comptes rendus, xxxviii, 304.

But in all these cases the compound MR was a salt scarcely soluble in water, and the more powerful solvent was an acid. Neither of these conditions is indispensable for the result. The following experiments will illustrate the general law in cases where 1st, the compound MR is soluble in water, though not so soluble as M'R', M'R, or MR'; 2nd, where M'R' is a neutral salt as well as MR.

1st—Sulphate of silver was dissolved in weak nitric acid; to a part of the solution nitrate of silver, and to another part sulphuric acid was added, with the production in each case of the crystalline sulphate.

Again, it was found that chloride of sodium had deposited from a solution of sulphate of sodium in hydrochloric acid; the liquid, which of course was saturated with the salt, and contained likewise free hydrochloric and sulphuric acids, and no doubt sulphate of sodium, was divided into two portions, and from each a crystallization of chloride of sodium was obtained by the addition, respectively, of sulphate of sodium and hydrochloric acid.

2nd—Where the solvent is a neutral salt. Chloride of lead was found to dissolve freely in acetate of sodium. Such a solution, saturated with the chloride, was prepared: it was divided into two parts; to the one neutral acetate of lead, and to the other chloride of sodium, was added, and in each case after awhile chloride of lead separated.

It appears, therefore, that the more general expression of the law deduced from theory, and given at the head of this section, is confirmed by experiment. Yet it is not to be expected that in every case the precipitate will actually make its appearance; for the formation of a double salt or the special solvent powers of the compound added may be a disturbing influence, and may give rise to anomalous exceptions.

Action of Acid Solvents, and Reciprocal Decomposition in Alcohol instead of Water.

When ferric phosphate was dissolved in hydrochloric acid, the paleness of the solution, and the increase of colour on the addition of more acid, both rendered it evident to the eye that the whole of the iron was not in the state of chloride. Indeed, a comparison of the colour gave ground for the belief that in a saturated solution, at least as much as 85 per cent. of the iron is actually held dissolved as phosphate in the acid present.* It became interesting to see whether this solvent action would take place in the absence of water; and if so, whether the same proportion between the different salts would be maintained. For this purpose, a solution of hydrochloric acid in absolute alcohol was prepared, and its power of dissolving dry ferric phosphate was tried. It dissolved a great deal, assuming a pale yellowish-green colour. Thus, one question was answered; but there still remained the inquiry whether the proportions of the several salts in solution were the same as when the experiment was made in water. This received a reply in the negative, showing that the nature of the liquid influenced the reciprocal action, for a comparison of the solution with one of ferric chloride in absolute alcohol showed that a very large quantity—probably 95 per cent.—of the iron must have been present as phosphate. Again, the alcoholic solution became much darker when diluted with water, which is not the case with the ferric chloride itself dissolved in alcohol. Another experiment made with this solution of the phosphate was the following:—a portion was divided into two equal parts; to the one was added some of the hydrochloric acid dissolved in alcohol, to the other the same bulk of pure alcohol. At first the two appeared of the same colour, but after awhile that containing the large excess of hydrochloric acid became decidedly deeper.†

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* See Chem. Soc., Qu. J., ix, 152.

† Some of the experiments described in this and the preceding section were brought forward at the meeting of the British Association at Leeds, in 1858, but the subject has been more fully worked out since.

Testimony from Diffusion Experiments.

I have already published* an account of an experiment showing that, from a mixture of equivalent proportions of chloride of sodium and nitrate of barium there diffused the four substances in such relative proportions as could only be explained on the assumption that each of the two acids had distributed itself between the two bases.† Professor Graham, in his recent paper "On Liquid Diffusion applied to Analysis," has described two experiments of a similar character; the one made with a mixture of chloride of potassium and sulphate of sodium, the other with equivalent proportions of chloride of sodium and sulphate of potassium; but the results are not so conclusive in favour of the law of reciprocal decomposition, for the numbers do not differ widely from such as might be given if all the chlorine were in combination with the potassium, and all the sulphuric acid with the sodium. Yet the accordance is not perfect, and the distribution of the four elements may be very different. One thing is conclusively shown by the perfect accordance of the two experiments, namely, that, in the words of Graham, "The acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of sodium is the same thing as a mixture of sulphate of potassium and chloride of sodium, when the mixtures are in a state of solution."‡

A Method of Quantitative Determination by means of Circular Polarization.

An argument in support of the law of reciprocal decomposition has already been drawn from an experiment made by Bouchardat,§ while examining the circular polarization of camphoric acid. He found that certain camphorates rotate the plane of polarization less than the acid itself, and that when one of these salts was supersaturated with hydrochloric acid, the solution did not exhibit so much polarizing power as it would have done had the whole camphoric acid been set free. Unfortunately, the experiment was not made with equivalent proportions of the different substances, and hence it has no quantitative value.

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* British Association Report, 1860, and Chem. News, Aug. 11th, 1860.

† The relative proportions in the diffusate expressed in equivalents were—sodium 1,253, chlorine 1,175, barium 812, nitric acid 892.

‡ Phil. Trans., 1861, 197.

§ Comptes rendus, xxviii, 319.

It occurred to me, however, that interesting numerical results might easily be obtained by taking advantage of the fact that different compounds of the same body rotate the plane of polarization differently; and just to test the possibility of this, I have made some determinations with two substances belonging to very different groups—nicotine and tartaric acid.

Nicotine gives a strong left-hand rotation, but when combined with hydrochloric acid it entirely loses this power.* A solution of known strength gave a rotation of $-14°$: it was mixed with an equivalent proportion of chloride of ammonium; the two odours of nicotine and ammonia were perceptible in the mixture, and when it was examined with the polariscope it indicated only $-10{\cdot}5$.

Hence it may be concluded, that sufficient nicotine to produce the wanting $-3{\cdot}5°$ of rotation had entered into combination with hydrochloric acid displacing of course an equivalent amount of ammonia. These numbers happen to have the common divisor 3·5. The four substances must therefore have been present together in solution in very nearly, if not exactly, the following proportions:

$\mathrm{Nic\,HCl} + 3\,\mathrm{NH_4Cl} + \mathrm{NH_3} + 3\,\mathrm{Nic}.$ $(\mathrm{Nic} = \mathrm{C_{10}H_7N}.)$

The experiment was repeated with chloride of sodium in place of chloride of ammonium. A rotation of $-28°$ was reduced to that of $-25°$ indicating the following composition for the mixture:

$3\,\mathrm{NicHCl} + 25\,\mathrm{NaCl} + 3\,\mathrm{NaO} + 25\,\mathrm{Nic}.$

As the nicotine has decomposed less chloride of sodium than chloride of ammonium, and its absolute tendency to unite with the hydrochloric acid must have been the same in both experiments, it follows that the soda must have a greater tendency to combine with the hydrochloric acid than the ammonia has, as compared with their tendency to remain in combination with water alone. In combination with hydrochloric acid 3 equivalents of ammonia, in fact, balance themselves against the nicotine, and as many as 8·3 equivalents of soda are required to do the same.

It is evident that the above experiment might be repeated with innumerable other salts, and tables of respective affinity might thus be drawn up. The method is also available for experimenting on the influence of the quantity of any of the constituents.

Tartaric acid gave results which are not so easily understood. It has already been observed that equivalent proportions of the isomorphous tartrates of potassium and ammonium have an equal influence on the polarized ray, and the same appears to be true of the sodium-salt. The amount of rotation is increased by the alkali, and apparently independently of whether it exists in the state of the neutral or acid-salt: thus:—

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* Indeed, when the acid was in great excess, Wilhelmy's observation of a slight indication of right-handed polarization seemed to be confirmed.

Tartaric acid	.. ..	= +10°
„	+ 1 equivalent of sodium (bitart.)	= +20·5
„	+ 2 equivalents „ (neut. tart.)	= +31·

Tartaric acid was mixed with an amount of citrate of sodium, sufficient to form the bi-tartrate of sodium, if it should decompose it entirely. The polariscope showed that a partial decomposition had ensued. Additional portions of the citrate were added, and an additional production of the tartrate resulted in each case. The numbers were—

Tartaric acid	.. ..	= +10°
„	+ $\frac{1}{2}$ citrate of sodium ..	= +14·4
„	+ 1 „ ..	= +18·5
„	+ 2 „ ..	= +23·

This result is in strict accordance with what was theoretically expected: the sodium has distributed itself between the two acids in certain proportions; namely, 8·5 to the tartaric, and 12·5 to the citrate, when equivalent proportions were employed; and when more citrate of sodium was added, more tartrate was produced.

Now, citric and tartaric are analogous acids, and perhaps the above is the true explanation of the phenomena observed; but when other salts of sodium were employed, results were obtained which showed some effect on the polarized ray that is not to be accounted for by such simple decompositions. Thus, with acetate of sodium—

Tartaric acid	.. ..	= +10°
„	+ 1 equivalent of acetate of soda	= +22°
„	+ 2 „ „	= +28°
„	+ 3 „ „	= +31°

When two or three equivalents of the acetate were employed, the results obtained are intelligible enough, but why should a single equivalent of acetate of sodium produce a greater increase of rotation than a proportionate amount of hydrate of soda would have done?

But there are greater anomalies still. When nitrate sulphate, or chloride of sodium, or chloride of ammonium is added to tartaric acid it actually reduces the rotating power. Thus:—

Tartaric acid .. .. = +10°
" + 1 equiv. nitrate of sodium .. = + 7°
" + 2 equiv. " " .. = + 5°
" + 2 equiv. sulphate of sodium .. = + 8°·5
" + 2 equiv. chloride of sodium .. = + 3°·5
" + 2 equiv. chloride of ammonium = + 4°

With sulphate of ammonia, a very slight increase of rotation was obtained.*

The cause of these phenomena has not yet been ascertained. It evidently will interfere with the use of tartaric acid for the purpose intended; but, doubtless other substances besides nicotine might be found to give trustworthy indications.

XLII.—*On the general occurrence of Titanic Acid in Clays, and the method employed to estimate it; on the Analysis of Iron Ores, and Siliceous Minerals containing Iron, the separation of Oxide of Iron from Titanic Acid, and the methods of estimating Iron.*

By Edward Riley.

Some time since the author presented to the Society a short communication,† pointing out the presence of titanic acid in a series of Welsh fire-clays, and at the same time proposed a new test for the metal. On a subsequent occasion also he pointed out, in a verbal communication, the errors that may arise from not carefully testing for the above acid, which is present, as will subsequently be shown, in all clays,—or at any rate its absence is the exception.

It is my object to bring before the Society, not only the method adopted for determining titanic acid, but at the same time to enter minutely into the various methods of analysis usually adopted with silicates, including also iron ores, and to notice some of the points which have, up to a recent period, been to me very unsatisfactory; it must, however, at the same time, be admitted that there are still many points which require investigation.

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* Since the above was written, I have found that Biot has observed the remarkable changes in the rotation of the polarised ray by tartaric acid caused by dilution, or by combination with various other bodies. His experiments throw no light on the question of reciprocal decomposition.

† Quarterly Journal of the Chemical Society, vol. xii, page 13.

Most chemists who have made the analyses of clays and minerals of a similar description, will agree that when the analysis is conducted in the way ordinarily advocated, many of the processes are very unsatisfactory.

The general method adopted for the analysis of a clay is to take from 15 to 20 grns. and fuse it with an alkaline carbonate; the fused mass is then dissolved in hydrochloric acid; the solution evaporated to dryness; the mass heated; and the silica separated by re-solution in hydrochloric acid; the insoluble matter obtained is regarded as silica, without any further treatment, or by some chemists it is either treated with a solution of hydrofluoric acid, or exposed to the vapour of that acid in Brunner's apparatus. After the silica is entirely dissolved, it is evaporated to dryness and ignited. Each of the last two methods is open to the objection that the greater portion of any titanic acid that may be present with the silica is converted into a fluoride of titanium, which is volatile and consequently lost in the subsequent ignition. This may be considered to be one of the reasons why titanic acid has not been found by chemists in all clays, although, generally speaking, a small residue is left when the silica from an analysis is heated as above, and the titanic acid may be detected with the blowpipe. This residue also contains traces of alumina.

Proceeding with the analysis, and precipitating by ammonia and well washing the precipitate, it is dissolved by hydrochloric acid (on the filter), and treated with a solution of pure caustic potash. In this process it will be observed that when the quantity of iron is small, instead of obtaining the ordinary and characteristic precipitate of peroxide of iron, a precipitate is obtained of a much lighter colour, and evidently a very impure peroxide of iron, so impure that the author has always found it necessary to ignite the washed and dried precipitate of iron and alumina, and redissolve it in acid, which process serves to separate a certain amount of silica which is always left in solution after the evaporation to dryness, and may be separated thus, or by a second evaporation to dryness, as shown in subsequent experiments. After separation of the silica by either of the two methods mentioned, a much more satisfactory separation of the iron and alumina may be made by potash. The oxide of iron, after separation is dissolved in hydrochloric acid and reprecipitated by ammonia; it is then generally weighed and considered to be pure peroxide of iron; but it very rarely dissolves completely in hydrochloric acid, sometimes leaving a residue which retains the form of the oxide; sometimes, but more rarely separating gelatinous silica. This residue, on being crushed, forms a powder which defies filtration, and in most of these cases consists of titanic acid. This has been found to take place more particularly in the analyses of clays and blast-furnace cinders or slags.

The following are the analyses of the blast-furnace cinders from the Dowlais iron works, showing the average composition of the cinder for a week's working. The cinders were taken as follows: cinder was taken from each furnace every day, and portions of the cinders finely pulverised, 200 grains of each being weighed out daily and kept separate in a bottle, labelled with the number of the furnace. At the end of the week the pulverised cinder in each bottle was again intimately mixed and analysed. The Table gives the result,—the numbers at the top being the numbers of the furnaces in blast at the time; column, " average of 13 furnaces," gives the analyses of a mixture of equal weights of pulverised cinder taken from each furnace at different times on one day.

In all the above analyses, the iron could not be obtained very pure, the impurity most probably consisting of a small quantity of titanic acid. The iron given in the analyses of blast-furnace cinders is generally too high. In many cases no manganese is given, and unless great care is taken, it is very difficult to obtain the oxide of iron even in a tolerable state of purity. These analyses are thought to be of sufficient interest to insert in the paper, as they are most probably the most extensive series of analyses of blast-furnace cinders yet made.

Average Composition of Blast-furnace Cinder (Slag) *during a Week's working of the Furnaces.*

	1	3	4	5	9	10	11	12	13	14	15	16	18	*Mean.*	Average of 13 Furnaces.
Silica	39·09	42·52	41·30	44·88	42·08	43·68	42·45	41·08	45·23	42·57	40·02	40·69	38·48	41·85	43·07
Alumina	17·14	14·96	16·21	15·51	14·19	16·25	14·30	13·65	11·55	13·12	14·71	14·82	15·13	14·73	14·85
Protoxide of Iron	2·07	3·62	2·65	6·91	2·35	1·33	2·04	1·29	3·08	3·48	2·52	2·19	0·76	2·63	2·53
Protoxide of Manganese .	1·15	1·50	1·10	1·67	1·59	1·15	1·22	1·02	1·02	1·18	0·91	1·04	1·62	1·24	1·37
Lime	31·95	30·04	30·55	23·81	31·55	28·57	30·89	34·32	32·09	31·35	32·27	32·60	32·82	30·99	28·92
Magnesia.............	4·31	3·95	4·42	4·38	4·67	4·42	5·32	4·65	3·78	4·44	5·47	4·63	7·44	4·76	5·87
Potash...............	1·98	2·06	2·26	1·98	1·73	2·21	2·04	1·75	1·53	1·79	1·72	1·71	1·92	1·90	1·84
Calcium	1·64	0·85	1·20	0·59	1·37	1·29	1·04	1·22	1·04	0·89	1·31	1·29	1·23	1·15	1·01
Sulphur	1·31	0·68	0·96	0·47	1·10	1·04	0·83	0·98	0·83	0·71	1·05	1·03	0·99	0·92	0·89
Phosphoric Acid	·22	0·41	0·13	0·43		0·10	0·10			0·17	0·25		0·15	0·15	traces.
	100·86	100·59	100·78	100·63	100·63	100·04	100·23	99·96	100·15	99·70	100·23	100·00	100·54	100·32	100·35
Metallic Iron	1·61	2·81	2·06	5·37	1·81	1·03	1·58	1·03	2·39	2·70	1·96	1·70	0·57	2·04	1 97

Furnaces 1 to 16, Common White Forge-pig. 18 Furnace, on Foundry-pig.

Should the mineral also contain phosphoric acid, a portion of that acid is invariably left with the oxide of iron, although by far the larger portion is found in solution with the alumina. The alumina is separated by acidifying the solution and boiling with chlorate of potash, to destroy any organic matter then precipitated by carbonate of ammonia; the phosphoric acid may be separated, after the alumina has been weighed, by dissolving in hydrochloric acid, adding tartaric acid, ammonia, chloride of ammonium, and a magnesian salt.

It is rare that clays contain an appreciable amount of manganese; any that they may contain will be partly precipitated with the iron and alumina; this is one of the many objections to the precipitation by ammonia. The lime is then separated by oxalate of ammonia and weighed either as carbonate or sulphate; this determination appears to be quite satisfactory. The magnesia is next precipitated by ammonia and phosphate of soda. In clays this mode of precipitation is often very unsatisfactory, the precipitate being quite flocculent, instead of exhibiting the characteristic crystalline appearance of the ammonio-magnesian phosphate. This may be due in some cases to a little alumina held in solution by the large excess of ammonia used to precipitate the oxide of iron and alumina, but there is reason to think that it arises also from other causes which it must be admitted have not yet received sufficient attention to enable one to speak positively respecting them.

Having briefly sketched the ordinary method employed for analysing clays, &c., I shall proceed to describe some experiments made in relation more particularly to the estimation and separation of titanic acid.

First, in treating the silica with hydrofluoric acid, to prevent the fluoride of titanium from volatilizing, sulphuric acid should be used; by this means the whole of the titanic acid with the silica may be obtained. It it, however, invariably mixed with alumina and minute traces of iron, as will be seen by the experiments detailed.

More titanic acid may be separated by again evaporating to dryness the filtrate from the silica, heating it strongly, redissolving in acid, and separating insoluble matter which consists of a mixture of titanic acid and silica with traces of alumina.

The results of numerous experiments lead me to the conclusion that the higher the temperature to which the fused mass is heated, after solution and evaporation to dryness, the greater will be the quantity of titanic acid left with the silica in the insoluble state, and therefore the smaller will be the quantity obtained in the second evaporation.

The oxide of iron obtained in the way just described in the analysis of clays, was tested as follows for titanic acid :—After it had been ignited and weighed, it was dissolved in hydrochloric acid, and insoluble matter was separated. This was burnt and treated in a platinum crucible with hydrofluoric and sulphuric acid, and the filtrate was reduced with a solution of sulphate of soda, added in large excess, sufficient to neutralise all the free hydrochloric acid. The solution was then boiled, and when nearly the whole of the sulphurous acid was expelled, a white precipitate was formed. The boiling was continued until a slight indication of sesquioxide of iron was seen ; the liquid was then rapidly filtered; the filter, which was not washed, was transferred wet into the platinum crucible containing the residue left on treating the mixture of silica and sesquioxide of iron with hydrofluoric acid,—then dried and burnt carefully at a low temperature; and the burnt mass was fused with bisulphate of potash, dissolved in cold water, and boiled after perfect solution. Immediately on boiling, a precipitate was formed, which, on filtering and testing, gave all the distinct reactions of titanic acid. The following are the results obtained from the analysis of a Welsh fire-brick :—

Some considerable portion of the brick was pounded up ; and a small portion was reduced to very fine powder, 19·23 grns. of which after ignition, was taken for analysis. It was fused over a Bunsen's burner with 6 or 7 times its weight of pure carbonate of soda, dissolved in hydrochloric acid, evaporated to dryness, and carefully heated. The silica was separated by solution in hydrochloric acid and dilution with water. The silica obtained weighed 12·09 grns. Silica treated with hydrofluoric and sulphuric acids, evaporated to dryness and ignited, left residue ·225. This residue was fused with bisulphate of potash, and dissolved in cold water, and the liquid after complete solution was boiled. After boiling some time, a distinct precipitate was formed, but hardly sufficient to weigh. The solution precipitated by ammonia yielded a precipitate of alumina containing a trace of iron, which weighed 0·21 grn. The filtrate from the silica was evaporated to dryness and heated; the residue dissolved as before in hydrochloric acid, and the insoluble residue separated: it weighed 0·36 grn. This residue treated with hydrofluoric and sulphuric acids, evaporated to dryness and ignited, left residue = 0·16 grn. This residue was fused with bisulphate of potash, and dissolved in cold water, and the liquid after solution was boiled; immediately on boiling, a precipitate formed, which was boiled for some time, allowed to stand for a night in a warm place, then collected on a filter, washed with water containing sulphuric acid, and weighed 0·105 grn., and this gave with microcosmic salt the characteristic reaction of titanic acid. The filtrate from the titanic acid was precipitated by ammonia, and gave a precipitate of alumina, which weighed ·075 grn., considered as Al_2O_3. The filtrate from the second evaporation for alumina and sesquioxide of iron was made nearly neutral with ammonia, and a moderate quantity of acetate of soda was added; the solution well boiled, and the basic acetates of iron and alumina were collected and washed, a few drops of acetate of soda being added at each washing; the precipitate was dissolved in hydrochloric acid and precipitated by ammonia, then washed, dried, ignited, and weighed: its weight was 6·16 grns. This was dissolved in hydrochloric acid, a flat-headed glass stirrer being used to crush the lumps. After complete solution, a residue of silica weighing 0·04 grn. was left and separated; the solution of sesquioxide of iron and alumina in hydrochloric acid was treated with pure potash in a platinum dish; and after boiling, the sesqui-oxide of iron was separated by filtration.

The sesquioxide of iron, after re-solution and precipitation by ammonia, was ignited and weighed: its weight was ·675 grn. This was dissolved in hydrochloric acid, a residue retaining the shape of the pieces of oxide of iron and coloured with it then remaining; these lumps were crushed and the boiling was continued until the residue was perfectly white; it was, however, so small in quantity, that no weight could be obtained for it on burning the filter. The filtrate was treated with bisulphite of soda in sufficient quantity to neutralize the whole of the free hydrochloric acid; it was then boiled till sulphurous acid could only just be smelt. After application of heat, a precipitate soon formed which gradually increased. When this precipitate began to assume a yellow tint from oxide of iron, it was rapidly filtered, and the filter, without being washed, was thrown into a platinum crucible, dried and burnt, then fused with bisulphate of potash. After fusion, the mass was dissolved in cold water, and then boiled. After boiling some time, a precipitate was formed, which was allowed to stand a night, then filtered and weighed as before described; the weight obtained was ·095 grn. The filtrate from the oxide of iron after treatment with potash, re-solution in hydrochloric acid, and re-precipitation by ammonia, was evaporated to a small bulk, and after treating with ammonia and phosphate of soda, gave indications of the presence of magnesia; $2MgO.PO_5$ obtained = 0·12 gr.

To separate alumina, the filtrate from oxide of iron was acidified with hydrochloric acid, chlorate of potash was added, the solution well boiled, and the alumina precipitated by ammonia and carbonate of ammonia, washed, dried, ignited, and weighed. Its weight was 5·535 grns. On dissolving it in hydrochloric acid, a similar quantity of silica was left = 0·03 grn. The filtrate treated with tartaric acid, magnesian salt, ammonia, and chloride of ammonium gave, after standing a night, a few distinct crystals of ammonio-magnesian phosphate, shewing the presence of a trace of phosphoric acid. The lime and magnesia were separated by the usual methods; with the magnesia there was a very small amount of the flocculent matter already alluded to. The lime weighed as sulphate gave 0·285 grn. The ammonio-magnesian phosphates weighed 0·56 grn.

The alkalies were determined by boiling the finely levigated brick with strong hydrofluoric acid in a gold crucible. 57·55 grns. taken after the brick had been thoroughly decomposed, was evaporated to dryness with sulphuric acid in a platinum dish; the mass, after being strongly heated, was well boiled in water, the lumps being crushed with a flat-headed glass rod; and the whole was transferred into a large beaker without filtration, and precipitated by ammonia and carbonate of ammonia. This method is adopted on account of the difficulty frequently experienced in separating the matter left insoluble in the boiling water, the fine particles usually clogging the filter. After separation of the precipitate by ammonia and carbonate of ammonia, the filtrate is evaporated to dryness, and ammoniacal salts volatilized; the residue is then treated with sulphuric acid and again evaporated to dryness, to drive off excess of sulphuric acid, then dissolved in water, treated with a solution of baryta in excess, and filtered. The usual method given is to treat with acetate of baryta, but it has always been found almost impossible to separate the sulphate of baryta by filtration, as it passes through the filter and filters very slowly; the use of hydrate of baryta entirely obviates this difficulty. The filtrate is acidified with acetic acid, evaporated to dryness and ignited; the carbonate of baryta and charcoal are separated by filtration; the carbonates of the alkalies are dissolved in water; the solution is acidified with hydrochloric acid and the alkalies weighed as chlorides: the chlorides obtained weighed 2·09 grns. The above method has always been found to yield most satisfactory results, and is, moreover, expeditious.

The potash and soda were separated in the usual way with bichloride of platinum, and 5·73 grns. platinum salt obtained.

Silica.

Silica by first evaporation	12·09	
Al_2O_3 with silica separated by HFl	0·21	11·88
Silica by second evaporation	0·36	
TiO_2 separated by HFl	0·16	0·20
Silica with iron and alumina	0·04	0·04
		12·12

Brick		Silica				
19·23	:	12·12	: :	100	:	63·02

Silica 63·02%

Titanic Acid.

Titanic acid from silica, second evaporation	0·105
Titanic acid from Fe_2O_3	0·095
	0·200

Brick		Titanic acid				Titanic acid
19·23	:	·200	: :	100	:	1·04

Titanic acid 1·04%

Alumina.

Alumina with silica		0·21
Alumina with titanic acid		0·075
Alumina separated from iron	5·535	
*Less silica with alumina	0·030	
	5·505	5·505
		5·790

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* This silica is not calculated as coming from the brick: it is thought to be due to the action of potash on the glass used.

Brick		Alumina				Alumina
19·23	:	5·79	: :	100	: :	30·11

Alumina 30·11%

Sesquioxide of Iron.

Magnesia with oxide of iron weighed as $2MgO.PO_5$ 0·12

$2MgO.PO_5$		$2MgO$		$2MgO.PO_5$		MgO
113·34	:	41·34	: :	0·12	:	0·043

Titanic acid with iron	0·095
Magnesia ,, ...	0·043
	0·138

Fc_2O_3

0·675 − 0·138 = 0·537

Brick		Fc_2O_3				Fc_2O_3
19·23	:	0·537	: :	100	:	2·79

Lime.

$CaO.SO_3$		CaO		$CaO.SO_3$		
68	:	28	: :	285	: :	0·11735
If 19·23	:	0·11735	: :	100	:	0·61

Lime 0·61%

Magnesia.

$2MgO.PO_5$ from Fc_2O_3	0·120
$2MgO.PO_5$ from CaO.	0·565
	0·685

2 $MgO.PO_5$		$2MgO$		$2MgO.PO_5$		MgO
113·34	:	41·34	: :	685	:	0·2498
Brick		MgO				MgO
If 19·23	:	0·2498	: :	100	:	1·29

Magnesia 1·29%

Alkalies.

$KCl.PlCl_2$		KO		$KCl.PlCl_2$		KO
244·2	:	47	: :	5·73	:	1·1028

Brick		KO				KO
57·55	:	1·1028	: :	100	:	1·92

KO		KCl		KO		KCl
47	:	74·5	: :	1·1028	:	1·748

Mixed chlorides KCl NaCl

$$2{\cdot}09 - 1{\cdot}748 = 0{\cdot}342$$

NaCl		NaO		NaCl		NaO
58·5	:	31	: :	0·342	:	0·1812

Brick		NaO				NaO
57·55	:	0·1822	: :	100	:	0·31

Tabulated Results.

Silica	63·02
Titanic acid . . .	1·04
Alumina	30·11
Sesquioxide of iron . .	2·79
Lime	0·61
Magnesia	1·29
Soda	0·31
Potash	1·92
Phosphoric acid traces .	
	101·09

DETERMINATION OF SILICA AND TITANIC ACID IN FIRE BRICKS.

Bricks in fine powder ignited before Fusion.

	Brick taken Grns.	Silica per cent.	Titanic Acid per cent.	Description of Brick	First Evaporation.			Second Evaporation.			
					Silica	Residue from Silica by hydrofluoric and sulphuric acid.	Titanic Acid in Residue	Alumina in Residue	Insoluble Residue	Titanic Acid in Residue	
1	35·975	65·11	1·05	Stourbridge (Hickman)	23·815	0·81	0·255	0·59	0·545	0·125	
2	20·90	63·42	1·05	do. (Rufford)	13·33	0·355	0·120		0·330	0·100	Alumina
3	28·39	60·49	0·60	Newcastle (Lucas)	17·49	0·535	0·17	0·40	0·435		0·155
4	27·11	60·60	0·42	Newcastle (Stephenson)	16·56	0·470	0·115	0·315	0·51		0·170
5	22·145	55·86	0·67	do. (Ramsay)	12·49	0·365	*		0·32	*	
6	21·965	62·96	0·96	Wortley, Leeds (Ingham)	14·03	0·475	0·15	0·335	0·375	0·06	
7	23·31	62·39	0·69	Harwarden, North Wales	14·555	0·32	0·03	0·225	0·475	0·13	
‡ 8	26·92	64·52	0·50	Yellow London Clay	17·54	0·405	†		0·275	†	
9	28·89	91·84	trace	Ewell Brick, Surrey	26·98	0·655 Alumina			0·210 Silica		
10	21·70	94·33	trace	Dinas Brick, South Wales	20·87	0·635			0·235		
11	23·43	75·16	trace	Black Alder, Devonshire	17·64	0·295			0·305		

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* In 5 the residues from evaporation 1 and 2 were weighed together, fused with bisulphate of potash, dissolved in cold water, and silica separated Silica = 0·245 ; titanic acid = 0·15.

† In 8 the same method adopted as in No. 5; silica obtained = 0·245, titanic acid = 0·135, alumina = 0·205.

‡ Clay dried at 300° Fahrenheit.

TABLE showing the results of various analyses in which Titanic Acid was found but not determined, except in No. 2. The Titanic Acid was not, in this analysis, determined by fusion with bisulphate of potash and precipitation by boiling, and is a little too high. In analyses 4, 5, 6, and 7 no indication of Titanic Acid was obtained when treating the soils by the ordinary methods; but special examination of the Sesquioxide of Iron obtained in the analysis revealed its presence; and, moreover, it was found that the soils contained Iserine, which was readily separated with a magnet.

		1	2	3	4	5	6	7
	Silica	59·21	27·75	55·16	48·53	49·17	47·10	48·01
1. American kaolin	Titanic acid	*	*	2·19	*	*	*	*
2. Bastard ironstone, technically known as "Jack"	Alumina	27·77	17·02	21·88	18·77	18·85	18·23	19·13
3. Blue clay from Wiltshire	Peroxide of iron	3·34	10·80	FeO 4·71				
4, 5, 6, and 7. Soils from the West India islands	Magnetic oxide of iron ..	..	..	..	9·58	9·77	10·81	9·31
	Manganese (red oxide) ..	..	1·42	..	0·55	0·55	0·75	0·49
	Lime	0·41	26·11	2·62	8·03	8·30	8·26	7·59
	Magnesia	0·41	11·84	1·51	4·62	4·11	5·38	4·03
	Potash	1·91	0·39	2·22	0·27	0·29	0·20	0·30
	Soda	traces of with Lithia	..	..	1·82	2·08	1·82	2·06
	Phosphoric acid	..	3·85	..	trace			
	Sulphate of lime	..	Sulphuric acid 0·51	Carbonic acid 2·40	0·20	0·12	0·20	0·20
	Combined water	6·87	Sulphur 0·14	6·04	3·33	3·12	3·24	3·85
	Moisture	0·24	0·15	..	3·24	2·35	2·49	4·20
	Organic matter	..	..	0·67	1·16	1·68	1·63	1·90
		100·16	99·98	99·40	100·10	100·39	100·11	101·07

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* Titanic acid was detected in very appreciable quantity, but not determined.

Table I shows the amount of titanic acid found in ten samples of fire-bricks and in a sample of ordinary London clay. The titanic acid was determined in the way already detailed; viz., evaporating the filtrate from silica to dryness, and heating. The method employed is perhaps not very accurate, as most probably in all cases the whole of the titanic acid is not separated, even by two evaporations to dryness, as will be seen by referring to the detailed analyses: some was found with the iron. It, however, shows the general occurrence of this acid in clays; in many the amount certainly exceeds one per cent. It will be observed that in columns 3 and 4 the whole of the titanic acid is with the silica; in some cases it has been obtained entirely in the second evaporation. This appears to be due to the temperature to which the fused mass is heated after solution and evaporation to dryness. The higher the temperature, the greater is the quantity of titanic acid obtained with the silica, and *vice versâ*.

Professor Miller, of King's College, London, has found 1·25 per cent. of titanic acid in Stourbridge clay, and Mr. D. Campbell has found it in several clays, by adopting the method above detailed.

The last three bricks are essentially silica bricks, and contain no clay. Practical men have informed me that the last brick is of inferior quality.

In these experiments, my evaporating dishes were coated on the interior with the peculiar metallic lustrous stain which so pertinaciously sticks to all vessels in which a titanate is dissolved in an acid or precipitated by boiling.

Preparation of pure Titanic Acid.

Pure titanic acid was prepared from the red nitride crystals from an old blast-furnace hearth; it was obtained unintentionally. The crystals, after having been freed as far as possible from iron by means, first, of dilute sulphuric acid, then of strong hydrochloric acids, were heated with a mixture of nitric and hydrochloric acids: the consequence was, that some considerable portion of the crystals was oxidized. The titanic acid was separated from the crystals by decantation, then washed and fused with bisulphate of potash, and thrown down from the solution of the fused mass by boiling. The washing of this precipitate was interminable, and the sulphuric acid could not be completely washed out. On drying it and igniting, some sulphuric acid was driven off, and on treating the ignited residue with water, no sulphuric acid was detected. From the above it would appear there is a difficultly soluble compound of sulphuric and titanic acid, which is continually washed out from the acid; and this is most probably the reason why the determination of titanic acid by precipitation from a boiling solution is not accurate.

Special Experiments with Titanic Acid.

2·78 grns. pure titanic acid were treated with hydrofluoric acid, and some sulphuric acid was added; the whole was evaporated to dryness, ignited, and weighed. Weight obtained 2·76 grns. It was then fused with bisulphate of potash, the fused mass dissolved in cold water, the solution boiled, and the titanic acid separated with the usual precautions. The titanic acid thus obtained weighed 2·535 grns. The filtrate, precipitated with ammonia, yielded a further quantity of titanic acid, weighing 0·12 grn., thus showing that the precipitation by boiling is not quite complete, but nearly so.

Experiments with Titanic Acid and Alumina.

Some pure alumina was prepared from alum by precipitating with ammonia, washing the precipitate, drying and igniting, re-dissolving in hydrochloric acid, and separating insoluble matter (a little silica), then re-precipitating by ammonia, washing, drying, and igniting.

Alumina ·22 and titanic acid ·08 were fused together with bisulphate of potash, the fused mass was dissolved in cold water, and the solution boiled. The titanic acid did not precipitate immediately, but in five or ten minutes; the alumina did not appear to affect the precipitation of the titanic acid.

No. 2. Experiments were made with 0·2 and 0·3 grn. of titanic acid with some alumina: the acid could always be detected, and alumina had no influence whatever on its precipitation. In fusing alumina with bisulphate of potash, care should be taken not to heat the mass too strongly, and drive off too much sulphuric acid, as in that case the fused mass becomes difficultly soluble in water, and in some cases, after solution, the alumina may possibly be precipitated by boiling from insufficiency of sulphuric acid. The precipitate cannot, however, be mistaken for titanic acid, and may be readily taken up by adding a little dilute sulphuric acid.

No. 3. *Quantitative experiment.* 1·135 alumina and 0·40 titanic acid were fused together with bisulphate of potash; the mass was dissolved in cold water, the solution boiled for some hours, and the titanic acid separated as usual, TiO_2 obtained $=$ 0·325. The alumina was precipitated from the filtrate with ammonia and carbonate of ammonia, the liquid filtered, the precipitate washed once or twice, re-dissolved in HCl, and re-precipitated. The quantity of alumina obtained was 1·185—

TiO_2	0·325
Al_2O_3	1·185
	1·510

thus showing a loss on the titanic acid and a gain on the alumina, as might be anticipated from previous experiments.

Experiments with Titanic Acid and Sesquioxide of Iron.

Pure sesquioxide of iron was obtained from protosulphate which had been recrystallised three times from distilled water, by oxidation with nitric acid and precipitation by ammonia. Great difficulty was, however, experienced in dissolving the ignited sesquioxide of iron in the bisulphate of potash by fusion; some of the pure protosulphate of iron was therefore used after it had been pounded and thoroughly dried between folds of bibulous paper.

Exp. 1. 6·30 grns. protosulphate of iron and 0·28 grn. titanic acid were fused with bisulphate of potash, dissolved in cold water and boiled; no precipitate was formed at first, but after ten or fifteen minutes' boiling, a precipitate began to form, which gradually increased in quantity, and was coloured with oxide of iron.

Exp. 2. 6·59 grns. protosulphate were fused with 0·15 titanic acid and bisulphate of potash as before. The mass was dissolved in cold water, and the solution boiled. After boiling several hours no precipitate was produced. After the liquid had boiled down to a small bulk in a covered beaker, it was filled up with water and boiled again for a considerable time, but no precipitate was produced.

Exp. 3. 4·29 grns. protosulphate of iron and 0·12 of titanic acid were fused with bisulphate of potash, dissolved in cold water, and boiled. After boiling for several hours, there were indications of the formation of a precipitate, but certainly nothing satisfactory, and not sufficient to indicate titanic acid, unless that substance was previously known to be present there. From the above experiments it is obvious why titanic acid has often been overlooked by chemists, and that oxide of iron should always be separated before testing for it.

Experiments with Titanic Acid and Ammonia.

2·425 grns. titanic acid were fused with bisulphate of potash, dissolved in cold water, and precipitated by ammonia; the precitate was washed, dried, ignited, and weighed, gave 2·58.

2·745 grns. of titanic acid were fused with bisulphate of potash and 200 grns. of pure chloride of ammonium added to the solution; it was then precipitated by ammonia, washed, dried, and ignited: it weighed 2·775.

From the above experiments, it is obvious that titanic acid is completely precipitated by ammonia, and that ammoniacal salts do not at all influence its precipitation.

My subsequent experiments with titanic acid relate more to its presence in iron ores and pig iron.

The method usually given in text-books for analysing iron ores or minerals containing much iron, is to dissolve them either in hydrochloric or nitro-hydrochloric acid, and separate the siliceous matter,—or, if the silica is in the soluble state, to evaporate the solution to dryness, re-dissolve in acid, and, after separating the silica, to precipitate the filtrate by ammonia. The precipitation by ammonia is open to many objections, which, in most analyses, are fatal to the accuracy of the results. These objections are, the precipitation of some manganese with the iron; the precipitation of the phosphoric acid as phosphate of lime, and of some carbonate of lime and magnesia. The precipitation of these last two bases may, in a great measure, be prevented by using great care; but not so with the former. An extensive experience in the analysis of iron ores and similar minerals has proved to me that phosphoric acid and manganese are very rarely indeed absent, phosphoric acid existing from a mere trace up to 4 per cent.

The difficulties above described may be obviated by nearly neutralising with ammonia the filtrate from silica or the insoluble residue (the latter may be either analysed separately, or the silica separated by fusion, and the second filtrate added to the first), then adding acetate of soda or ammonia in excess, and boiling the solution for some time: the oxide of iron and alumina are thereby completely precipitated, together with all the phosphoric acid, which is entirely free from manganese, lime, and magnesia. This process also completely precipitates titanic acid if present in the ore. The precipitate must be washed with boiling water, and a few drops of acetate of soda or ammonia added every time it is washed: if this is not done, the precipitate clogs the filter, the washing becomes tedious, and some of the iron passes through the filter. This precipitate should then be dissolved in hydrochloric acid, re-precipitated by ammonia, dried, ignited, and weighed. Experience has proved to me that this is necessary, as in all cases the precipitate contains silica, which is, in a great measure, separated by re-dissolving the ignited precipitate in acid. The filtrate from the small amount of silica may be treated with potash, and alumina separated by acidifying with hydrochloric acid the filtrate from the oxide of iron, boiling with chlorate of potash, and adding carbonate of ammonia: the precipitate is then to be ignited and weighed. This alumina contains by far the larger proportion of phosphoric acid, but not all, as some is invariably left with the iron. The phosphoric acid may be separated from the alumina by dissolving it in hydrochloric acid and adding tartaric acid, ammonia, sal-ammoniac, and a magnesian salt. The oxide of iron is re-dissolved in hydrochloric acid, precipitated by ammonia, and weighed: if tested for phosphoric acid, it will always be found to contain that acid, if present in the ore. Should titanic acid be present, the oxide of iron is, after dissolving in hydrochloric acid, reduced with bisulphate of soda, the excess of sulphurous acid is boiled off, the solution nearly neutralised with ammonia, acetate of soda or ammonia added in excess, and the solution boiled. The titanic acid is then completely precipitated, and may be obtained pure by fusing with bisulphate of potash as before described.

The filtrate from the precipitate by acetate of soda is treated in a flask with bromine and ammonia, and heated gently, then boiled, whereby the whole of the manganese is most completely and readily separated as peroxide, which may be filtered off rapidly and weighed, after washing and drying, as Mn_3O_4. The filtrate is heated in the ordinary manner for lime and magnesia. When an iron ore is analysed as above described, the sesquioxide of iron is not obtained in a pure state. The separation of the sesquioxide from alumina by potash is most unsatisfactory; and it will be found that the oxide of iron is too high, no reliance can be placed on weighing iron as sesquioxide after it has been separated from alumina by potash. In proof of this it will be necessary to detail some special experiments made on the determination of iron, the results of which prove that the only sure and safe method of determining it is by a standard solution either of bichromate of potash or permanganate of potash; or rather, it is never safe to consider sesquioxide of iron as such, until it has been dissolved and treated either by Penny's method or Marguerite's.

Careful experiments were made with pure sulphate of iron, the same being used as previously described. 6 pints of solution of bichromate of potash was prepared by dissolving 270 grns. of the salt in distilled water, and 140 grns. pure carbonate of potash added to make it alkaline; 1500 grns. burette was used. A standard solution was prepared by dissolving the finest bright-drawn iron wire in dilute hydrochloric acid in a 30 oz. flask closed with a funnel; after perfect solution of the iron wire, it was filled up with cooled boiled distilled water, making in all rather more than a pint of solution.

1	Iron wire	6·525 grs.	required meas.	solution	1285 ∴ 1000 = 5·0778
2	,,	7·075	,,	,,	1393 ∴ 1000 = 5·0789

With the above solution, the iron was determined first in the pure protosulphate; then in the sesquioxide obtained from the protosulphate, after it had been precipitated by ammonia, and weighed as Fe_2O_3.

Iron by Standard Solution of Bichromate of Potash.

No. 1.	$FeO.SO_3$	30·66	required measures	1220	= iron per cent.	20·207
,, 2	,,	34·615	,,	1375	,,	20·172
,, 3	,,	48·265	,,	1925	,,	20·189
,, 4	,,	27·29	,,	1087	,,	20·227
					Mean	20·199

Theory gives 20·144 per cent.

The protosulphate of iron was dissolved in water; the solution acidified with a moderate quantity of hydrochloric acid, and diluted with rather more than a pint of cooled boiled distilled water.

Iron weighed as Fe_2O_3.

No. 1. $FeO.SO_3$	33·155	gave Fe_2O_3	9·575	= iron per cent.	20·215
„ 2 „	50·04	„ „	14·45	„	20·213
„ 3 „	40·28	„ „	11·655	„	20·254
„ 4 „	30·22	„ „	8·735	„	20·233
				Mean result	20·229

The sulphate of iron was dissolved in water, peroxidized with nitric and hydrochloric acid, precipitated by ammonia, dried, ignited, and weighed.

Iron determined in Sesquioxide by Standard Solution of Bichromate of Potash.

The above sesquioxide was dissolved in strong hydrocholoric acid, transferred into a 30 oz. flask filled two-thirds full with distilled water, and about as much sulphite of soda added as would cover a shilling, the liquid being gradually heated, and boiled till no smell of sulphurous acid was discernible, then cooled in water and treated with the standard solution.

No. 1. Fe_2O_3	9·575	required meas. solution	1315	= iron per cent.	20·141
„ 2 „	14·45	„ „	1991	„	20·141
„ 3 „	11·655	„ „	1604	„	20·12
„ 4 „	8·735	„ „	1200	„	20·165
				Mean	20·142

In dissolving the sesquioxide of iron in acid, some gelatinous silica separated in every case; it was, however, very minute in quantity, but distinctly discernible.

Comparing the results obtained by determining the iron directly by standard solution, determining the iron by weighing as Fe_2O_3, and again determining iron in the Fe_2O_3 by reduction and standard solution, we have—

	By standard solution direct.	Weighing as Fe_2O_3.	Determining. Fe in Fe_2O_3.
Iron per cent.	20·199	20·229	20·142

Theory 20·144.

From the above experiments, it is obvious that with a pure salt of iron, containing no other base, the determination of iron by weighing as sesquioxide is accurate, and that its determination by standard solution of bichromate of potash, either in the pure proto-salt, or in the peroxide of iron from it, agrees in every respect with the former.

When, however, potash is used, or any quantity of fixed base is in solution, the determination of iron by weighing as sesquioxide is inaccurate; this will be seen by the following direct experiments. Moreover, the results of a very long experience have proved to me that the sesquioxide of iron obtained in an analysis of an iron ore is always too high; and it is very rare indeed that the determination of iron by weighing as Fe_2O_3, can be made to agree with the determination by standard solution.

Experiments with Sesquioxide of Iron, and its determination when mixed with Alumina and Titanic Acid.

Pure sesquioxide of iron, the same as prepared from the protosulphate previously alluded to, was used, and a standard solution of bichromate of potash, 1000 grns. of which were equivalent to 5·28 of iron.

10·39 grns. pure sesquioxide, dissolved in hydrochloric acid, and precipitated by ammonia, gave 10·435 Fe_2O_3. This re-dissolved in hydrochloric and reduced with sulphite of soda, required 1386 measures of the standard solution of bichromate, equal to 10·454 F_2O_3.

Separation of Sesquioxide of Iron and Alumina by Potash.

The potash used for the following experiments was carefully tested, and on operating on some quantity, traces of silica could be detected; it was, however, an inappreciable quantity. A little alumina was also detected, but too small in quantity to affect the results; the same oxide of iron and alumina, prepared as described, were used. Sesquioxide of iron 14·47 and alumina 2·225 were weighed out and dissolved in strong hydrochloric acid; the solution was transferred to a large platinum bowl, and well boiled; the sesquioxide of iron separated by filtration, dissolved in hydrochloric acid, re-precipitated by ammonia, then dried and ignited, weighed 14·705 grns. This was re-dissolved in acid, and found to contain a quantity of silica too minute to be weighed; the solution was reduced with sulphite of soda; the iron determined by standard solution required 2142 measures.

1000 measures = 4·75 = Iron 10·174 or Fe_2O_3 14·53.

The filtrate from the oxide of iron, after separation by potash, was acidified with hydrochloric acid, and well boiled with chlorate of potash, then precipitated by carbonate of ammonia, and the precipitate was well washed, dried, ignited: it weighed 2·195, which, on re-dissolving in acid, left no residue of silica.

Taken.	Obtained by precipitation.	Obtained by standard solution.	Excess.
Fe_2O_3 14·47	14·705	14·53	0·275
Al_2O_3 2·225	2·195		

Assuming the above experiment to represent the analysis of an iron ore, and that 20 grns. had been taken, the difference in the actual amount of sesquioxide of iron present and that obtained would be 0·275 × 5 = 1·375, or a difference of more than one per cent. in the amount of iron.

Separation of Sesquioxide of Iron and Titanic Acid.

Fe_2O_3 taken 14·51; TiO_2 0·21. The titanic acid was fused with bisulphate of potash, dissolved in cold water, and added to the dissolved solution of the oxide of iron in strong hydrochloric acid; the mixture was precipitated with ammonia, dried after washing, and ignited: it weighed 14·765. On dissolving it in hydrochloric acid, no indications whatever were observed that titanic acid was present, as the oxide of iron dissolved completely. The sesquichloride of iron was diluted with water, and reduced with sulphite of soda, the excess of sulphurous acid being boiled off; the solution was nearly neutralised with ammonia, and acetate of soda added in excess; the liquid was then boiled; the titanic acid was precipitated, together with a little sesquioxide of iron, and was rapidly filtered off; the precipitate of the filter was not washed, but dissolved in hydrochloric acid; the iron again reduced as before, and the titanic acid precipitated by nearly neutralising with ammonia and adding excess of acetate of soda. The titanic acid was thus obtained nearly free from iron. After filtering, without washing the filter, it was transferred into a platinum crucible, dried, then burnt, fused with bisulphate of potash, dissolved in cold water, and the titanic acid was precipitated by boiling, and collected on a filter, with the precautions already described. The quantity obtained was 0·20 grn. The sesquioxide of iron was determined by adding all the filtrates together, oxidizing with nitric acid, and precipitating by ammonia. The quantity obtained was 15 grns.; this, on being re-dissolved in acid, was accidentally lost.

In this case, the excess was: 15·00 − 14·51 = 0·49. Every care was used to have the sesquioxide of iron perfectly washed.

Separation of Sesquioxide of Iron, Alumina, and Titanic Acid.

Taken Fe_2O_3 11·08; Al_2O_3 2·58; TiO_2 0·20; the oxide of iron and alumina were dissolved in hydrochloric acid; the titanic acid was fused with bisulphate of potash, dissolved in water, and added to the solution of iron and alumina. The whole were then precipitated together, and weighed 14·07 grns. On dissolving this acid no indication whatever of titanic acid was obtained, but there was left a slight gelatinous residue of silica, which weighed ·08. This was separated and treated with hydrofluoric acid and a little sulphuric acid, but left no residue; the filtered solution was boiled with pure potash in a platinum dish, and sesquioxide of iron separated. The alumina determined in a similar manner to that described in experiment 1, weighed 2·485 grns.; when re-dissolved in acid it left no appreciable residue of silica. The sesquioxide of iron on the filter, together with the titanic acid, was re-dissolved in acid and re-precipitated by ammonia, washed, dried, and ignited; it weighed 11·63 grns.; this, on re-dissolving in acid, left a residue of 0·15 silica, which gave no appreciable residue on treating with hydrofluoric and sulphuric acid. The solution from the silica was reduced with sulphite of soda, and treated in precisely the same manner as in experiment 2. The titanic acid weighed 0·20 grns. The filtrates from the separation of titanic acid by the acetate were mixed together, peroxidized with nitric acid, and the sesquioxide of iron was precipitated by ammonia; it weighed 11·215 grns., and was found to contain a trace of silica. The last filtrate from titanic acid was not added to the first two filtrates, as it was found, on testing it, to contain only a trace of iron, which did not appear quite pure sesquioxide. The sesquioxide of iron, after solution in acid, was treated with a standard solution of bichromate of potash, of which it required 1645 measures. 1000 = 4·75 = Fe 7·813, or Fe_2O_3 11·16. In this case, the excess in the oxide of iron is not very great; it is, however, occasionally obtained pure, or rather, nearly so; but this is the exception.

Having detailed the above experiments, which prove the errors that arise from weighing iron as sesquioxide, and considering it pure without testing it by standard solution, I shall now give the results of an analysis of an iron ore, very carefully made, the results being in duplicate; and at the same time to show the very grave errors which arise from precipitating the iron and alumina in an iron ore by ammonia. A dispute arose some time since concerning the yield of an iron ore, in which samples were sent to an eminent provincial chemist and myself; but no agreement could be made on the yield of the samples; it was therefore agreed to take a large sample, have it dried, finely pulverized, and send a portion to each. The samples were identically the same in a fine powder. The analyses made bore not the slightest resemblance the one to the other, as seen by the following Table, the differences being entirely due to the dangerous practice of precipitating the solution of the ore by ammonia.

The method of analysis already described was adopted, and the following results were obtained :—

	grns.
Hygrometric water.	
No. 1. 38·54 grns. of ore lost, after drying at 212°, Fahr. .	1·21
„ 2. 38·09 „ „ .	1·24
Water, total amount, combined and hygrometric, determined by heating, in a glass tube drawn out at end, and absorbing water in a chloride of calcium tube :—	
No. 1. 21·145 grns. of ore yielded of water at a red heat	2·14
„ 2. 18·170	1·80
No. 1. By the action of hydrochloric acid (with little nitric) on the ore :—	
24·52 grns. of ore, dry at 212°, Fahr., gave of insoluble residue	4·55
„ Soluble silica	0·06
„ Sesquioxide of iron, alumina, and phosphoric acid, weighed together	15·25
„ Contained soluble silica	0·02
„ Sesquioxide of iron	13·84*
„ Sesquioxide of iron contained phosphoric acid .	0·175
„ Alumina	1·55
„ Alumina contained phosphoric acid. . .	0·47
„ Manganoso manganic oxide	0·05
„ Sulphate of lime	3·10
„ Pyrophosphate of magnesia	0·89

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* Silica separated from sesquioxide of iron ·06 not calculated in analysis.

ANALYSIS OF OOLITIC IRON ORES.

	1.	2.
Clay and sand	18·80	18·42
Organic matter	0·60	0·60
Iron pyrytes	0·35	0·45
Peroxide of iron	49·97	47·98
Protoxide of iron	5·36	5·31
Oxide of manganese	0·20	0·44
Alumina	5·09	6·48
Lime	5·20	5·02
Magnesia	1·32	1·32
Phosphoric acid	1·71	1·88
Carbonic acid	4·61	4·93
Combined water	6·92	7·15
	100·13	99·98
Metallic iron, per cent.	39·39	37·95
Clay and sand contained—		
Silica	16·47	15·77
Alumina	1·28	1·27
Peroxide of iron	0·34	0·24
Potash	9·28	0·28

Precipitated by Ammonia.	3″.	Results compared. 3.	Results compared. 4.
Extraneous water	19·20		
Water of composition	11·07	13·70	7·03
Metallic iron	33·93	41·99	37·71
Oxygen	14·50	17·94	15·58
Silica	15·35	18·99	18·61
Carbonate of lime	2·66	3·29	9·12
Alumina	2·26	2·79	6·48
Magnesia	0·44	0·54	1·32
Phosphoric acid	slight	trace.	1·80
Oxide of manganese	—	—	0·32
Excess of carbonic acid	—	—	0·76
Organic matter	—	—	0·60
Iron pyrytes	—	—	0·40
Loss	0·59	0·73	—
	100·00	99·97	99·73

1, 2, 3 and 4 dry at 212° Fahrenheit.

	grns.
The insoluble residue gave of—	
24·52 grns. silica, containing a trace of titanic acid	3·91
,, Sesquioxide of iron	·085
,, Alumina	·315
,, Traces of lime and magnesia	
Analysis 2. By the action of hydrochloric acid, with a little nitric, on the ore :—	
20·74 grns. of ore, dried at 212° Fahr., gave insoluble residue	3·76
,, Sesquioxide of iron, alumina and phosphoric acid, weighed together	12·745
,, Soluble silica in above	0·02
,, Iron determined in the above by standard solution of bichromate of potash : measures required, 1600 = Fe_2O_3	11·017
,, Standard 1000 measures = 4·82Fe.	
,, Determination of phosphoric acid. Mean results % 1·80; therefore 20·74 grns. of ore contain PO_5	0·37
,, The total quantity of oxide of iron and alumina, &c. 12·745 grns. diminished by Fe_2O_3 11·017, PO_5 0·37 and SiO_3 0·02, leaves alumina	1·338
,, Manganoso-manganic oxide	0·090
,, Sulphate of lime	2·490
,, Pyrophosphate of magnesia	0·74
The insoluble residue gave of—	
Silica	3·10
Iron and alumina 0·41, containing Fe_2O_3	0·05
Alumina by loss 0·36—0·10 silica contained in this precipitate	0·26

Determination of Iron direct.

19·75 grns. of ore, dried at 212°, required 1556 measures of standard solution of bichromate of potash, whereof 1000 = 4·82 Iron =	37·97 p. c.
23·90 grns. of ore, dried at 212°, required 1877 measures of standard solution of bichromate of potash, whereof 1000 = 4·82	37·85 ,,
From above analysis	37·78 ,,

Determination of FeO by dissolving the ore in a large flask in a current of pure carbonic acid, diluting with cold boiled distilled water, and estimating the protoxide of iron with standard solution of bichromate of potash.

61·73 grns. of ore, dried at 212°, required 535 measures of standard solution of bichromate.

52·51, dried at 212°, required 450 measures of standard solution, whereof 1000 measures = 4·82 iron.

Determination of Phosphoric Acid.

No. 1. 61·55 grns. of ore, dry at 212°, gave $2MgO.PO_5$. 1·71
" 2. 42·78 " " " . 1·27

The phosphoric acid was determined by the method proposed by A. Dick; viz.: by dissolving the ore in hydrochloric acid, filtering off insoluble matter, reducing the filtrate with sulphite of soda, and boiling off all free sulphurous acid, oxidizing a small portion of the solution with nitric acid, nearly neutralizing with ammonia, adding acetate of soda and boiling. All the phosphoric acid is then precipitated, together with a small amount of sesquioxide of iron, some of which goes down as basic acetate. The precipitate was collected and dissolved in hydrochloric acid; tartaric acid, ammonia, chloride of ammonium, and a magnesian salt were added; the liquid was allowed to stand two nights; and the precipitate was collected, filtered, and weighed as $2MgO.PO_5$.

Determination of Sulphur.

No. 1. 66·51 grns. of ore dry at 212°, gave $BaO.SO_3$. 0·92
" 2. 46·28 " " " . 0·84

The sulphur was determined by fusing the ore with a mixture of pure carbonate of soda and nitre in a gold crucible, dissolving in dilute acid, evaporating to dryness, and separating insoluble matter by redissolving in dilute hydrochloric acid, then precipitating by chloride of barium.

Determination of Carbonic Acid.

No. 1. 103·19 grns. of ore, dry at 212°, gave CO_2 . . 4·76
2. 65·24 " " " . . 3·22

The carbonic acid was determined by dissolving the ore in a small flask provided with a safety funnel, and collecting the gas in potash-bulbs after drying it by passing through a chloride of calcium tube.

Organic Matter and Alkalies.

104·37 grns. of ore, dried at 212°, were dissolved in hydrochloric acid and silica, and the insoluble residue was separated, carefully detached from the filter, and treated in a platinum dish with hydrofluoric acid until all the silica was volatilized, and the clay was entirely decomposed; the partially dissolved mass was then treated with strong hydrochloric acid, and well boiled, and the organic matter left undissolved was collected on a tared filter and weighed . . .	0·63
The filtrates from the silica, and the filtrate from organic matter, were mixed together and precipitated by ammonia, and the alkalies were determined as already described for clays. Alkaline chlorides obtained .	0·48

In the analysis of iron ores, the author has entirely given up the use of potash; the sesquioxide of iron, alumina, and phosphoric acid are weighed together, as in analysis No. 2, and then the mixture is dissolved in hydrochloric acid; any silica it may contain is filtered off; the iron is determined by standard solution, and the sesquioxide thus obtained is deducted from the mixed precipitate; then, by calculation, the phosphoric acid contained in it is ascertained by a special determination made for this acid; this is also deducted, and the residue is alumina. Estimations by loss are generally objectionable, but a long experience has proved to me that the above method is the most reliable.

Titanium in Pig Iron.—This metal has only been detected satisfactorily on one occasion in a sample of very siliceous grey pig, containing $4\frac{1}{4}$ per cent. of silicon; it was found in the following manner:—A large quantity of the pig was dissolved in hydrochloric acid to test for metals; the insoluble silica was separated by filtration, and the filter treated with nitric and hydrochloric acids, again filtered, and the solution, on being evaporated to drive off nitric acid, was unintentionally allowed to go to dryness. On redissolving in hydrochloric acid, some insoluble residue was left, which was separated by filtration, and treated, after burning in a platinum crucible, with hydrofluoric and sulphuric acids—it was not silica: on fusing with bisulphate of potash, it gavethe distinctive and characteristic reactions of titanic acid. In testing pig iron for titanium, care must be taken, as the author has in many cases obtained precipitates in testing for titanic acid, which he considered to be the acid, but on further examination found to be perphosphate of iron. In dissolving pig iron in acids, if there is much silica and phosphorus, some phosphide of iron is almost sure to be left with the silica; and this, after being treated with hydrofluoric and sulphuric acids, is left as a residue of perphosphate of iron, which was, in some cases, confounded with titanic acid, until a more intimate knowledge of its properties had been obtained.

Titanium in Iron Ores.—It is a mistake to suppose that titanic acid is left with the silica in the analysis of an iron ore, or that it is completely separated by evaporation to dryness; a considerable amount of titanic acid is dissolved by strong hydrochloric acid. In an iron ore containing from 20 to 30 per cent. of titanic acid, nearly the whole of the titanic acid was dissolved in the hydrochloric acid, and only a small amount obtained with the silica. The author hopes shortly to be able to lay before the Society some experiments made with rutile in the manufacture of steel, and also some details as to the presence of titanium in iron and steel: his present opinion is that it does not alloy to any considerable extent with iron.

XLIII.—*On Berberine—Contributions to its History and Revision of its Formula.*

By J. Dyson Perrins, F.C.S.

The objects of this paper are to announce some new sources for the alkaloid berberine, to describe several of its salts hitherto unnoticed, and to review the formula proposed by Fleitmann.

The chemical history of berberine is somewhat remarkable, and it will not be out of place here to refer briefly to it. The first notice of this body has hitherto been attributed to Buchner and Herberger, who discovered it in *Berberis vulgaris*, in 1835. They erroneously regarded it as a weak acid, rather than as a powerful organic base, and Buchner's formula has long been abandoned. I find however that Chevallier and Pelletan deserve honourable mention as being the first observers of berberine; they accurately described it under the name of Zanthopicrite in 1826.

More recently Fleitmann[*] published an account of "Berberine and some of its Salts," clearly establishing its basic character, and propounding a formula replacing that which had resulted from the previous labours of Buchner. Fleitmann's formula has obtained general acceptance,[†] varied however by Gerhardt, who, on theoretical grounds, proposed the addition of a single equivalent each, of hydrogen and oxygen. In addition to many of the *Berberideæ*, various other sources for this alkaloid, so remarkable for its beautiful yellow colour, have been discovered by Boedeker[‡] in *Cocculus palmatus*, the calumba root of pharmacy, belonging to the natural order, *Menispermaceæ;* by Stenhouse[§] in *Cœloclin polycarpa*, natural order *Anonaceæ*, an African wood from Sierr Leone; by myself[||] in *Coscinium fenestratum*, natural order *Menispermaceæ*, a root from Ceylon; by myself[¶] also in *Xanthorriza apiifolia*, natural order *Ranunculaceæ*, a North American plant; by Mahla[**] in *Hydrastis Canadensis*, another of the *Ranunculaceæ*, also a North American plant, common in the United States, the rhizome of which is used in American pharmacy.

Some time before the publication of Mahla's paper, I had noted the occurrence of berberine in *H. Canadensis;* indeed it was through that observation I was led to make the present inquiry.

I can recommend *H. Canadensis*, which may be readily obtained in this country, as an excellent and available source for berberine; it yields about four per cent. of the crude alkaloid.

In addition to the sources already named, I have now to announce the following new ones: it seems unnecessary to describe the methods employed to isolate the alkaloid—they were always founded upon its solubility in alcohol and the sparing solubility of the nitrate in solutions acidulated with nitric acid.

In the India Museum, there is a yellow dye-wood from Upper Assam, called by the native name *Woodunpar;* of this I obtained a specimen through the courtesy of Dr. J. Forbes Watson; I find that berberine constitutes its yellow-colouring principle. I regret that I have been unable to ascertain the proper botanical name; from its structure it probably belongs to the order *Menispermaceæ*.

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[*] Chem. Gaz. 1847 vol. v. p. 129; Ann. Ch. Pharm. lix. 60.

[†] Except by *Kemp*, vide Chem. Gaz. v. 5, p. 209, who proposed a formula which has found no support; his platinum determinations agree with Fleitmann's and my own, but most unaccountably his carbon determinations of the platinum-salt are about two per cent. higher than those of any other chemist before or since.

[‡] Chem. Gaz. vol. vi. 302.

[§] Pharm. J. Trans. 1855, vol. xiv. p. 455.

[||] Phil. Mag. [4] iv. 99.

[¶] Pharm. J. Trans. 1862, vol. iii. 567.

[**] Silliman's Journal, 1862, vol. xxxiii. p. 43.

A woody root called *Raiz de São Joao*, or St. John's root, from Rio Grande, I believe twice imported into this country, and of which a specimen has been kindly given to me by Daniel Hanbury, Esq., F.L.S., &c., abounds in berberine; in this instance also I am unable to give the botanical designation. I gladly avail myself of this opportunity of expressing my sense of the kind assistance I have received from my friend Mr. Hanbury in the course of this inquiry. Amongst numerous rare specimens, this gentleman has favoured me with, is a yellow bark from the Botanical Museum at Kew, of which little appears to be known; it is simply named "*Pachnelo* tree—*yellow dye—Bogotà.*" This bark I find to be very rich in berberine, of which it yielded nearly seven per cent. of its weight. If further inquiry should show that pachnelo-trees are plentiful in New Grenada or other districts in South America, a most valuable source for berberine will be secured.

The next source for this alkaloid which I have to announce is one of considerable interest; it is the root of *Coptis Teeta* or *Mahmira*, a ranunculaceous plant of Hindostan and China, highly prized on account of its tonic properties, and known in the bazaars of India as *Mishmee bitter*. There is an historical notice of this root from the pen of the late Dr. Pereira.* He regards it as probable that *Coptis Teeta* is a remedy of great antiquity, in fact a classical medicine, used in ancient Greece and described by certain Greek and Arabian authors; in more recent times known in Europe under another name, but its origin not suspected; the first accurate notice of the root by any modern writer was given by Dr. Wallich, from whose account I quote:—"Mishme Teeta is the name by which the drug is designated among the Mishmees and Lamas in the mountainous regions bordering upon Upper Assam. The Chinese call it *Honglane*; among these three nations it is in great estimation and universal use as a powerful tonic and stomachic. Quantities are sent down to Assam in neat little baskets, with open meshes made of narrow slips of ratan or some such material, and measuring three to four inches in length by two and a half in breadth. Each basket contains about an ounce of small pieces of the root from one to three inches long; they are nearly cylindric, uneven, scabrous, more or less curved, of a greyish-brown colour, and varying in thickness from the size of a crow-quill to double that diameter. The root is perfectly dry and brittle; occasionally a few fibrillæ are issuing from one end; the inside is hard, somewhat cellular, the outside of a dingy, yellow colour. The taste is intensely and purely bitter, very lasting and with only a very slight aroma. On mastication, the root tinges the saliva yellow or gold-coloured, it possesses no smell whatever."

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* Pharm. J. Trans., 1851, vol. xi. 294

This account well describes a quantity of the root which I received from the East India Museum, through the kindness of Dr. J. Forbes Watson. I soon ascertained that the active principle of *Coptis Teeta* is berberine, in which the root abounds. I obtained from it eight and a half per cent., which is the largest amount yet met with, nor will it probably ever be surpassed. I did not obtain any other crystalline substance from this root.

Lastly, I have succeeded in establishing the fact that Zanthopicrite obtained from *Zanthoxylum Clava Herculis,* by Chevallier and Pelletan,* in 1826, is no other substance than berberine, and that consequently they must be considered as the first observers of this body. My friend, Mr. Hanbury, again assisted my inquiry, by furnishing me with some of the bark of *Z. clava Herculis,* according to Dr. Julius Martiny, a German pharmacologist of eminence, this bark is somewhat peculiar, from its highly laminated texture, splitting readily into thin plates like garden bast; this is noticed by the French authors, and altogether the careful description they give exactly applies to the bark which I have examined. The botanical synonyms are *Z. clava Herculis,* Linn.; *Z. Carolinianum,* Gaertner; and *Z. Caribæum,* Lamarck; it is quite necessary to particularize this, in order to prevent the confusion consequent upon the last-named botanist applying the specific term *Z. clava Herculis* to a tree which is totally distinct.

The French chemists do not appear to have attempted the ultimate analysis of their zanthopicrite, but they have carefully noted several of its properties and re-actions, not omitting the somewhat unusual deportment of this body with sulphide of potassium. My own results have clearly proved the identity of zanthopicrite and berberine.

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* Journ. de Chemie med., 1826, vol. ii. 314; Note sur le *Zanthoxylum des Caraibes* ou *Clavalier des Antilles* par MM. Chevallier et Gabriel Pelletan. This bark is used in the West Indies as a febrifuge.

Z. clava Herculis belongs to the natural order *Rutaceæ,* and furnishes the first recorded example of berberine being a product of any plant of that order.

I now proceed to detail the numerical results I have obtained. It seems unnecessary to state in each case, from which plant I have prepared the salt for analysis; suffice it to say, that the whole of the sources now first announced are included.

It is not without some hesitation that I allow myself to question the conclusions of chemists of the eminence of Fleitmann, Boedeker, and others; but my own results are so accordant with each other, the number of analyses I have made, and the variety of combinations I have examined are so considerable, that I feel not only justified in proposing an alteration of the formula, but, indeed, compelled to do so. Perhaps, my hesitation is lessened by the recollection that, on a former occasion, I acquiesced in Fleitmann's formula, and even supposed that it was confirmed by my analysis of the hydrochlorate, and by a platinum determination; but later experience has shown me that the hydrochlorate is not suited for ultimate analysis, as by pretty long exposure to a temperature of 100°C., or thereabouts, it undergoes some decomposition, the colour changes permanently, and much of it becomes readily soluble in cold water, yielding a red solution; in these respects, it differs from the undried salt, thus proving that some alteration by heat has taken place. The pure alkaloid itself is equally unsuited for analysis, and for similar reasons, indeed I find it not easily prepared in a state of purity. With regard to the platinum determinations of some previous chemists, it is evident that impure products have been examined. I find that very many crystallizations are necessary before any of the salts of berberine can be pronounced pure. I must also state that the numerical results of Fleitmann agree with mine in many cases, and support the formula I propose rather than his own.

Fleitmann's formula is $C_{42}H_{18}NO_9$.* A glance at these numbers will suggest great doubts of their accuracy, the number of oxygen equivalents and the sum of those of hydrogen and nitrogen being indivisible by two; Gerhardt observed this, and proposed to represent berberine by $C_{42}H_{19}NO_{10}$? His alteration has the effect of increasing the atomic weight, which my results point out as being already too high. The formula I propose is $C_{40}H_{17}NO_8$, which, with Gerhardt's, is equally free from theoretical objection, and I hope to show that it is fully borne out by abundant analytical proof.

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* C = 6. O = 8; for the sake of comparison, these values will be retained through this paper.

As the platinum-salt possesses many advantages for determining the composition of the alkaloid, I have from time to time examined it; it may be prepared with ease in a pure state, in consequence of its great insolubility; like every other combination of berberine, it may be obtained in minute crystalline needles by precipitating a hot dilute solution of any berberine salt with bichloride of platinum. When collected, the precipitate should be washed with cold water, until the washings, upon the addition of iodide of potassium, give no evidence of the presence of platinum; it may then be dried at once in the water-oven without any fear of decomposition, and it burns without difficulty.

Analysis of *Chloroplatinate of Berberine*:—

No. 1.—4·451 grains, burned with lead-chromate, gave
7·250 „ carbonic acid, and
1·369 „ water.

No. 2.—6·604 grains gave
10·714 „ carbonic acid, and
2·033 „ water.

No. 3.—5·681 grains, burned with soda-lime for nitrogen determination, gave
1·127 „ platinum.

No. 4.—5·449 grains gave, on careful ignition,
·988 „ platinum.

No. 5.—2·733 grains gave
·679 „ platinum.

No. 6.—5·455 grains gave
·990 „ platinum.

No. 7.—3·879 grains gave
·705 „ platinum.

No. 8.—3·781 grains gave
·686 „ platinum.

No. 9.—3·350 grains gave
·610 „ platinum.

No. 10.—5·091 grains gave
·932 „ platinum.

No. 11.—4·310 grains gave
·790 „ platinum.

No. 12.—5·880 grains gave
1·075 „ platinum.

Percentage composition—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
C	44·42	44·24										
H	3·41	3·42										
N			2·80									
Pt.				18·13	18·19	18·14	18·17	18·14	18·20	18·31	18·33	18·28

leading to the formula $C_{40}H_{17}NO_8.HCl.PtCl_2$ as will be seen from the following comparison:—

	Calculated		Perrins. mean.	Fleitmann. mean.
40 equivs. carbon	240	44·35	44·33	44·39
18 „ hydrogen ..	18	3·33	3·41	3·50
1 equiv. nitrogen ..	14	2·59	2·80	
8 equivs. oxygen	64	11·83		
3 „ chlorine ..	106·5	19·68		
1 equiv. platinum ..	98·6	18·22	18·21	18·11
1 equiv. chloroplatinate of berberine	541·1	100·00		

It should be stated that every determination was from a different crystallization of the salt, often prepared at long intervals.

From this, one of the most precise methods known, it will be seen that not only my own results, but Fleitmann's also, point to the adoption of the proposed formula; that of the German chemist requiring but 17·53% of platinum, or less by 0·7%; and of carbon 44·83%, or more by 0·4%, a divergence from the foregoing results which appears to me, all but decisive on the point of its inaccuracy.

Chloroaurate of Berberine.

This combination was examined as possessing an advantage even over the platinum-salt for the object in view, owing to the high combining weight of gold.

On adding terchloride of gold to the hydrochlorate or other salt of berberine, the double gold-salt immediately falls as an amorphous brown-coloured precipitate, quite insoluble in water; it is purified for analysis by washing with water, and dissolving in boiling dilute spirit, from which it crystallizes on cooling in chestnut-brown needles, which may be dried at 100°C. without decomposition, it burns without difficulty :—

No. 1.—8·209 grains gave, on combustion,
10·687 „ carbonic acid, and
2·004 „ water.

No. 2.—6·862 grains gave
8·932 „ carbonic acid, and
1·706 „ water.

No. 3.—5·600 grains gave, on ignition,
1·643 „ gold.

No. 4.—7·988 grains gave
2·317 „ gold.

No. 5.—7·950 grains gave
2·316 „ gold.

In 100 parts—

	1.	2.	3.	4.	5.
Carbon	35·50	35·50			
Hydrogen..	2·71	2·76			
Gold			29·34	29·00	29·13

corresponding to the formula

$$C_{40}H_{17}NO_8.HCl.AuCl_3,$$

as the following comparison will show :—

	Calculated.		Experiment.
40 equivs. carbon	240	35·57	35·50
18 „ hydrogen ..	18	2·67	2·74
1 equiv. nitrogen....	14	2·08	
8 equivs. oxygen	64	9·49	
4 „ chlorine....	142	21·05	
1 equiv. gold	196·6	29·14	29·16
1 equiv. double gold-salt	674·6	100·00	

Fleitmann does not appear to have examined this salt, but according to his formula, the amount of gold should be only 28·26%, or nearly one per cent. less.

The next combination to be described is interesting, as belonging to a class that I do not remember to have seen noticed before, viz., the double hyposulphites of silver and the alkaloids.

Hyposulphite of Berberine and Silver is precipitated in a yellow amorphous pulverulent form, when to a cold neutral solution of a salt of berberine is added hyposulphite of soda, saturated, ornearly so, with any silver-salt. The precipitant may be prepared by adding nitrate of silver to solution of hyposulphite of soda, so long as the precipitate first formed is redissolved; it must be filtered and used while fresh, as in time the silver is gradually deposited as sulphide.

The double berberine-salt is insoluble in water, but readily so in spirit, and in solution of hyposulphite of soda; it is decomposed by ebullition, with separation of sulphide of silver. To prepare the salt for analysis, I add the argentine solution to nitrate of berberine dissolved in weak spirit, while hot; the double salt crystallizes out on cooling in minute prisms of a pure lemon-yellow colour; they are readily washed with water, and the air-dried salt does not decompose or alter in colour at 100° C. Upon careful and prolonged ignition, nothing is left but perfectly white metallic silver :—

No. 1.—5·958 grains, burned with usual precautions, gave
9·381 ,, carbonic acid, and
1·730 ,, water.

No. 2.—6·553 grains gave
10·380 ,, carbonic acid, and
1·910 ,, water.

No. 3.—5·56 ,, grains, burned with carbonate of soda and oxide of mercury, gave
4·646 ,, sulphate of baryta.

No. 4.—6·625 grains gave, on ignition
1·290 ,, silver.

No. 5.—5·997 grains gave
1·165 ,, silver.

In 100 parts—

	1.	2.	3.	4.	5.
Carbon....	42·94	43·20			
Hydrogen..	3·22	3·24			
Sulphur ..			11·47		
Silver				19·47	19·42

leading to the formula

$$C_{40}H_{17}NO_8,HO.S_2O_2,AgO.S_2O_2,$$

as is shown by the following comparison :—

	Calculated.		Experiment.
40 equivs. carbon	240	43·16	43·07
18 „ hydrogen ..	18	3·23	3·23
1 equiv. nitrogen....	14	2·52	
14 equivs. oxygen ...	112	20·16	
4 „ sulphur	64	11·51	11·47
1 equiv. silver	108	19·42	19·45
1 equiv. double silver salt	556	100·00	

Bichromate of Berberine.—This salt has been described by Fleitmann as an amorphous substance. I have to remark that it may be obtained in orange-yellow needles by adding bichromate of potassium to a boiling and very dilute solution of a salt of berberine—the crystals separate entirely on cooling. This salt is extremely insoluble in excess of the precipitant and in cold water, but it may be recrystallised from a large quantity of hot water. It burns readily, and the green oxide of chromium may thus be determined with exactitude. This salt agrees in constitution with the bichromates of ammonia, lepidine, chinoline, &c., in containing only one atom of water :—

No. 1.— 6·094 grains gave, on combustion,
11·964 „ carbonic acid, and
2·198 „ water.

No. 2.— 4·432 grains gave
8·747 „ carbonic acid, and
1·624 „ water.

No. 3.— 8·490 grains gave, on incineration,
1·480 „ sesquioxide of chromium.

No. 4.—10·149 grains gave
1·770 „ oxide of chromium.

In 100 parts—

	1.	2.	3.	4.
Carbon	53·54	53·87		
Hydrogen	4·00	4·07		
Oxide of chromium			17·43	17·44

agreeing with the formula*

$$C_{40}H_{17}NO_8HO,2CrO_3$$

as is shown by the following comparison :—

	Calculated.		Experiment.
40 equivs. carbon	240	53·86	53·71
18 „ hydrogen	18	4·04	4·04
1 equiv. nitrogen..........	14	3·14	
12 equivs. oxygen	96	21·55	
1 equiv. oxide of chromium. (Cr_2O_3)	77·6	17·41	17·43
1 equiv. bichromate of berberine	445·6	100·00	

Nitrate of Berberine.—This salt has been described by Fleitmann: it is so little soluble in slight excess of nitric acid, that it admits of repeated crystallizations without perceptible loss. It dissolves pretty readily in water, but separates most completely upon the addition of a few drops of dilute nitric acid. To insure its purity, I find it is necessary to crystallize repeatedly until the colour of the mother-liquor is no longer darkened by excess of ammonia, which may be considered as a proof that solutions of pure berberine do not assume a red colour upon the addition of an alkali; any change of colour is evidently due either to impurity or it points to some alteration in the alkaloid. Nitrate of berberine is to be preferred as the source from which to prepare every other combination; it may be subjected for any length of time to 100° C. without losing its fine yellow colour, having in this respect a great advantage over the hydrochlorate. For analysis, I finally crystallized it from hot water to get rid of every trace of free acid.

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* Fleitmann's analysis of this salt does not agree very closely with mine, which is not surprising, as he did not obtain it in crystals, but examined an amorphous powder of difficult purification; his view of its constitution is unsatisfactory. and appears to be erroneous.

I found the nitrate admirably adapted for analysis, as the following concordant results will show :—

No. 1.—5·002 grains gave, on combustion,
11·032 ,, carbonic acid, and
2·058 ,, water.

No. 2.—5·213 grains gave
11·504 ,, carbonic acid, and
2·149 ,, water.

No. 3.—4·516 grains gave
9·970 ,, carbonic acid, and
1·868 ,, water.

No. 4.—4·046 grains gave
8·927 ,, carbonic acid, and
1·673 ,, water.

No. 5.—4·535 grains gave
10·014 ,, carbonic acid, and
1·913 ,, water.

In 100 parts—

	1.	2.	3.	4.	5.
Carbon	60·15	60.18	60·21	60·17	60·22
Hydrogen ..	4·57	4·58	4·57	4·59	4·68

corresponding with the formula

$$C_{40}H_{17}NO_8.HNO_6,$$

as is shown by the following comparison :—

	Calculated.		Experiment.	Fleitmann.*
40 equivs. carbon..........	240	60·30	60·19	59·89
18 ,, hydrogen........	18	4·52	4·60	4·68
2 ,, nitrogen	28	7·03		
14 ,, oxygen..........	112	28·15		
1 equiv. nitrate of berberine..	398	100·00		

Hydrobromate of Berberine may be prepared by adding bromide of potassium to solution of nitrate of berberine, acidulated with acetic acid. It instantly falls as a yellow precipitate soluble in pure water, but insoluble in excess of bromide of potassium; from its solution in hot water or spirit, it falls in yellow acicular crystals, which bear a temperature of 100° C. without decomposition, but assume a bright orange colour :—

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* Fleitmann's carbon determinations were 59·64 and 60·15 per cent.

No. 1.— 5·450 grains, on combustion, gave
11·505 „ carbonic acid, and
2·125 „ water.

No. 2.— 4·900 grains gave
10·360 „ carbonic acid, and
1·914 „ water.

No. 3.—13·308 grains gave
5·936 „ bromide of silver.

In 100 parts—

	1.	2.	3.
Carbon	57·57	57·66	
Hydrogen	4·33	4·34	
Bromine			19·00

corresponding with the formula

$$C_{40}H_{17}NO_8.HBr$$

as is here shown :—

	Calculated.		Experiment.
40 equivs. carbon	240	57·69	57·62
18 „ hydrogen ..	18	4·32	4·33
1 equiv. nitrogen ..	14	3·37	
8 equivs. oxygen	64	15·39	
1 equiv. bromine ..	80	19·23	19·00
	416	100·00	

The salt dried in vacuo lost 5·75 per cent. of water at a temperature of 100° C., which amount agrees pretty closely with three equivalents, and consequently it may be represented by

$$C_{40}H_{17}NO_8.HBr.3aq.$$

Hydriodate of Berberine.—Like other combinations of this alkaloid, the hydriodate occurs in the form of minute yellow acicular crystals: it is easily prepared in the same manner as the preceding salt, substituting, of course, iodide of potassium for the bromide; the hydriodate is extremely insoluble, whether in pure water or in excess of the precipitant. It does not lose weight at 100° C. nor suffer any decomposition or change of colour.

Highly dilute solutions of berberine yield a precipitate on the addition of iodide of potassium. For analysis it is best prepared by precipitating a weak solution of nitrate of berberine in hot dilute spirit, with iodide of potassium. Crystals fall immediately: they may be washed upon a filter with water for some time without loss:—

No. 1.—5·905 grains gave, on combustion,
11·199 ,, carbonic acid, and
2·094 ,, water.

No. 2.—6·495 grains gave
12·329 ,, carbonic acid and
2·304 ,, water.

No. 3.—5·205 grains gave
2·602 ,, iodide of silver.

No. 4.—7·005 grains gave
3·514 ,, iodide of silver.

In 100 parts—

	1.	2.	3.	4.
Carbon	51·72	51·77		
Hydrogen ..	3·92	3·96		
Iodine......			27·02	27·12

corresponding with the formula

$$C_{40}H_{17}NO_8.HI$$

as the following table shows :—

	Calculated.		Experiment.
40 equivs. carbon	240	51·83	51·75
18 ,, hydrogen	18	3·88	3·94
1 equiv. nitrogen	14	3·03	
8 equivs. oxygen	64	13·83	
1 equiv. iodine	127	27·43	27·07
1 equiv. hydriodate of berberine	463	100·00	

Hydriodate of Biniodo-berberine, or Teriodide of Berberine?

This compound is formed when a slight excess of iodine is added to solution of any berberine salt, either in water or spirit: in the latter solvent it dissolves on heating, and crystallizes in the form of transparent red-brown prisms, which are of extremely sparing solubility either in cold alcohol or in water; in the latter liquid they may be considered quite insoluble, as they do not impart any tinge of colour to it.

This compound is not a substitution-product; nitrate of silver rapidly removes all the iodine, with formation of nitrate of berberine. For analysis, the substance was dried at 100°C. and burned with chromate of lead and a pretty long column of reduced copper-turnings; this salt dried over oil of vitriol does not lose weight at 100 C.

No. 1.— 6·832 grains gave
8·405 ,, carbonic acid, and
1·585 ,, water.

No. 2.— 6·120 grains gave
7·502 ,, carbonic acid, and
1·424 ,, water.

No. 3.—10·877 grains ignited with pure lime gave
10·733 ,, iodide of silver.

in 100 parts—

	1.	2.	3.
Carbon	33·55	33·43	
Hydrogen	2·57	2·58	
Iodine			53·36

corresponding with the formula

$$C_{40}H_{17}NO_8I_2HI$$

as is shown by the following comparison :—

	Calculated.		Experiment
40 equivs. carbon	240	33·47	33·49
18 ,, hydrogen	18	2·51	2·57
1 equiv. nitrogen	14	1·95	
8 equivs. oxygen	64	8·93	
3 ,, iodine	381	53·14	53·36
1 equiv. of hydriodate of biniodo-berberine ..	717	100·00	

I have retained the nomenclature adopted by Anderson for the teriodides of codeine and papaverine, with which this salt is evidently analogous; perhaps the name I suggest is the more correct, and I prefer it; but, as Anderson has previously remarked, the rational constitution of these substances is obscure.

I have now to describe a remarkable compound of Iodine with berberine, having certain analogies with the quinine-salt termed Herapathite. When dilute solution of iodine in iodide of potassium is added to solution of any salt of berberine in hot spirit, *carefully avoiding an excess of iodine,* the new substance speedily makes its appearance in the form of brilliant green spangles, which increase in quantity as the solution cools; they are invariably accompanied by crystals of hydriodate of berberine, or by the red salt last described, nor have I been able to devise any method of preparation by which this admixture can be wholly prevented. The formation of this new body is an excellent test for the presence of berberine; minute quantities may be detected by this reaction. Its occurrence seems to be determined whenever tincture of iodine containing hydriodic acid is added to solution of any salt of berberine in hot weak spirit, scrupulously avoiding excess of iodine; rapid agitation appears to promote its formation, and the presence of any impurity to interfere with it. Like Herapathite, it bears a strong resemblance to particles of the elytra of cantharides, and to murexide; under the microscope it is seen to consist of crystals of a variety of forms, but I believe all derived from a rhombic prism; the larger crystals are wholly opaque; many of the smaller ones however are sufficiently thin to allow of the passage of light, which assumes a red-brown hue, sometimes inclining to violet; but the light is perfectly polarized, in this respect also resembling Herapathite, with which its optical properties are obviously similar.

I obtained this compound with the smallest admixture of hydriodate, and in the largest crystals, by heating in a strong bottle, solution of berberine in alcohol of 90%, with addition of iodide of ethyl, to 100°C.; upon cooling, the bottle contains crystals of hydriodate of berberine, but if exposed to full sunshine for one or two hours, the crystals pass into the green salt now under notice. When the change appears to be complete, the bottle must be removed from the sunshine, or else the crystals will further pass into the red iodine-salt last described. Exposure to diffused daylight for some days may be substituted for sunshine;

but with every precaution, I have not been able to obtain the substance free from foreign crystals. It is not easy to see why this iodide of ethyl process succeeds better than others; probably the gradual development of free iodine is important. By this method I have obtained crystalline plates one-fifth of an inch in length by about half that breadth—of course, perfectly opaque. When removed from the solution and well washed with weak spirit, to remove adhering iodine, they have a blackish-green colour with a fine metallic lustre, yielding a nearly black powder, which does not decompose at 100°C.

I am inclined to believe that in composition this body is identical with the red salt, and differs from it only in molecular arrangement,—certainly it passes with the utmost facility into hydriodate of biniodo-berberine, and *vice versâ*. Nitrate of silver removes the iodine with the same ease, and with the same formation of nitrate of berberine.

A carbon and hydrogen determination yielded respectively 35·65 and 2·78 per cent., or numbers a little higher than they should have been, doubtless attributable to the presence of hydriodate of berberine. An iodine determination gave me less than the theoretical quantity, which was to be expected; one cogent reason why I believe the proper designation of these salts to be hydriodate of biniodo-berberine, rather than teriodide of berberine, is founded upon the observation that the green compound is not formed in the presence of any substance which decomposes hydriodic acid, e.g. nitrous acid; the presence of ordinary sweet spirit of nitre, which always contains free nitrous acid, entirely prevents its formation.

The foregoing analytical results will, I imagine, be considered as almost conclusive proof that the proposed formula for berberine is the true expression for that base; and consequently the previous belief that this alkaloid contains 42 equivalents of carbon must be abandoned.

Upon the chemical constitution of berberine, I have no new remark to offer, beyond the observation, that the action of iodide of ethyl results only in the formation of hydriodate. I did not obtain any ethylated compound; but the substitution-products of berberine well deserve careful study. Fleitmann has glanced at a sulphur-compound; I believe it will be found that more than one such exist; the same may be said with regard to nitric acid, bromine, chlorine, &c. Fleitmann has noticed what may be termed the ultimate action of nitric acid; but there appear to be several intermediate products, the knowledge of which will doubtless reward future inquiry.

Berberine evidently occupies a position among the vegetal alkaloids, of great interest in a scientific point of view—a position far more prominent than has hitherto been assigned to it; if noticed at all in our Manuals, it is dismissed in half a dozen lines. From inquiries, which can be termed little more than superficial, its occurrence has been shown in numerous plants, belonging to no less than five of the great vegetal families—the natural orders of the botanist—nor can it be doubted that many other sources yet remain to be discovered; its geographical distribution, even in the present state of our knowledge, is all but universal; it is to be found in almost every country, certainly in every climate, and in these respects it claims precedence over all the other alkaloids.

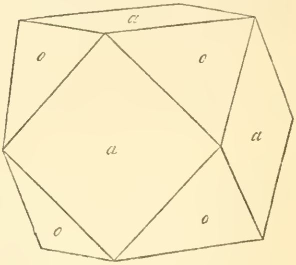
As regards its usefulness to man, I believe its importance is not yet fully recognised. Though it has been long used as a fine yellow dye, more especially for animal tissues, its chief claims to usefulness do not reside in its application to the economic arts—doubtless its therapeutic effects merit much careful investigation. Natural instinct has pointed out its value for the alleviation of human suffering, to nations widely separated and enjoying different degrees of civilisation. The polished Greeks, the semi-barbarous nations of Hindostan and China, the North American Indians, and the natives of tropical Africa, have been all impressed with the medicinal value of berberine. In the West India Islands and in American pharmacy, its virtues have long been recognised, though derived from different plants, and veiled under erroneous names: certainly, it holds a place in European pharmacy, but one of little prominence; yet it seems to possess properties scarcely inferior to quinine itself. Various medical writers have insisted upon its advantages as a remedial agent; their arguments it would be out of place here to recapitulate; but I am persuaded that nature has not placed berberine in nearly every country without some adequate purpose; there are evidences that its value is becoming better understood amongst ourselves, and I confidently anticipate that ere long its reputation will be greatly increased.

XLIV.—*On a Complex Cyanide of Iron, Copper, and Potassium.*

By William J. Wonfor,

Student in the Laboratory of the Museum of Irish Industry.

This complex cyanide crystallised in the form of reddish brown crystals, from a solution which had been employed in electro-plating, and was afterwards set aside and left undisturbed for several months; during that time the crystals made their appearance.



These crystals, for the measurement of which I am indebted to Professor W. H. Miller, of Cambridge, belong to the cubic system; they are combinations of the cube and octohedron. They resemble the annexed figure, the faces marked *a*, being the faces of the cube, and the faces marked *o*, those of the octohedron.

The angle between perpendiculars to any two adjacent faces *a*, is 90°.

The angle between perpendiculars to any two adjacent faces *o*, is 70° 30′.

The angle between perpendicular to any face *a* and an adjacent face *o*, is 54° 44′.

The following estimations give the amount of water lost in the water-bath:—

I.—1·936	grm.	lost ·0825	grm.	or 4·2613	per cent.
II.—0·9175	,,	,, ·0400	,,	,, 4·3590	,,
III.—0·5355	,,	,, ·0675	,,	,, 4·3310	,,
		Mean	-	- 4·3171	,,

For the estimation of the copper, iron, and potassium, the cyanide, dried at 212° F., was decomposed by Nordhausen sulphuric acid; the copper was first precipitated by sulphide of hydrogen; and the sulphide of copper was redissolved in nitric acid, precipitated by potash, and estimated as oxide in the usual way. The iron was peroxidised, then precipitated by ammonia, and weighed as peroxide; whilst the potassium was weighed as sulphate of potash.

The analyses yielded the following results:—

I.—1·2972 grm. gave ·1966 grm. of Fe_2O_3 & ·6245 grm. of $KOSO_3$
II.—1·6431 „ „ ·2494 „ Fe_2O_3 & ·4718 „ CuO
III.—1·0735 „ „ ·3111 „ CuO & ·5168 „ $KOSO_3$

The nitrogen was estimated by Will and Varrentrapp's method, the substance employed being dried at 212° F.:—

I.—·888 grm. gave 2·447 grm. of $NH_4Cl,PlCl_2$ = ·15345 of N.
II.—·7895 „ 2·180 „ „ = ·1365 „

The organic analyses were made with chromate of lead, the substance employed being dried at 212° F.:—

I.—·4836 grm. gave ·2617 grm. of CO_2 & ·0616 grms. HO.
II.—·6410 „ „ ·345 „ „ & ·0828 „ „

	I.	II.	Mean.
Iron	10·609	10·625	10·617
Potassium....	21·608	21·611	21·609
Copper	23·139	23·230	23·184
Nitrogen	17·284	17·289	17·287
Carbon	14·758	14·680	14·719
Hydrogen	1·461	1·435	1·448
Oxygen......	11·141	11·130	11·136
	100·000	100·000	100·000

These results may be expressed by the following calculations:—

		Calculated.
2Fe	56	10·113
3K	117	21·127
4Cu	126·8	22·896
7N	98	17·696
14C.............	84	15·168
8H	8	1·444
8O	64	11·556
	553·8	100·000

This salt lost in the water-bath 4·3171 per cent.; had it lost 4·73, it would correspond to 3 equivalents of water; this would give 11 as the total number of equivalents; but I am inclined to think, from a determination of the water which I made by combustion in an undried portion, that the true number of equivalents of water is 10. These calculations lead to the formula:—

$$(3KCy.2FeCy.2Cu_2Cy) + 10HO.$$

It is evidently the same substance that Bolley found deposited in a copper solution which had been employed in electro-plating; and subsequently Moldenhauer, seems to have formed it—if we may trust the incomplete analysis he has given—by boiling a solution of subcyanide of copper in a solution of ferrocyanide of potassium.

XLV.—*On the Formation of the Iodides of the Alcohol-radicles from Boghead Naphtha.*

By C. Greville Williams, F.R.S.

The possibility of passing from the bibasic to the monobasic radicles, by the addition of hydrogen to an olefiant, through the medium of a hydracid, was first shown by M. Berthelot. The reaction with hydriodic acid is represented by the equation:—

$$C^nH^n + HI = C^nH^{n+1} I.$$

This reaction has been of the greatest service to me in pursuing my researches upon the hydrocarbons produced during the distillation of Boghead coal.

My first experiments were made to ascertain whether homologues of benzole and of marsh gas would, by dilution, prevent the action of the hydracids on the comparatively small quantity of the olefiant present. With hydrochloric acid this would appear to be the case. I then resorted successfully to fuming hydriodic acid, having a density between 1·8 and 1·9; a less concentrated acid has little action.

The following process appeared to yield the iodides more readily than any other yet tried. The naphtha, of a boiling point corresponding with that of the olefiant to be experimented on, was placed in a flask with a neck three or four feet long. About half the bulk of fuming hydriodic acid having been added, the mixture was cohobated for two or three hours. The neck was then cut off and replaced by a bent tube connected with a condensing apparatus. On applying a gentle heat, the hydrocarbons unacted on slowly distilled away. The more volatile portion having in this manner been removed, the distillation was carried on in a current of steam, until the distillate began to sink in water. The receiver was then changed and the product collected apart.

By proceeding in the manner described, I have obtained from Boghead naphtha the iodides of amyl, œnanthyl, capryl, and pelargonyl. It is evident, therefore, that Boghead naphtha may now be made to yield an almost infinite variety of products, some of them belonging to organic groups, which have, hitherto, almost escaped investigation.

The quantities of the iodides produced up to the present time, have been too small to allow direct analyses to be made: it became necessary, therefore, to employ some reaction by which a small quantity of iodide might be made to yield a comparatively large amount of a substance capable of being purified and analysed. For this purpose nothing appeared more suitable than the compound ammonias, because a very small amount of base could be made to yield a large quantity of platinum-salt.

With this intention the iodides were sealed up in strong tubes with a large excess of alcoholic ammonia, and heated to 100° C., for twelve hours. On opening the tubes and supersaturating the fluid with hydrochloric acid, a small quantity of oil remained undissolved, which was carefully removed. The soluble portion was then evaporated nearly to dryness, to expel the alcohol and traces of hydrocarbons. The solution distilled with excess of hydrate of potassium, yielded ammonia and an oily base. On adding a great excess of solid hydrate of potassium to the mixture, the alkaloid separated almost entirely, and, after distillation, was dissolved in hydrochloric acid and treated with an excess of chloride of platinum. The strength of the solution was so adjusted that no immediate precipitation took place. By exposing the dish containing the mixture, to a surface of sulphuric acid for a few hours, the salt was generally procured in fine crystals. In this manner the platinum-salts of amylamine, œnanthylamine, caprylamine, and pelargonamine were prepared. The second and fourth of these bases are entirely new, and it is believed that none of them have ever before been procured from a homologue of olefiant gas.

I have not, as yet, been able to obtain any iodide of caproyl.

Platinum-salt of Amylamine.

Amylene is present in such small quantity in Boghead naphtha, that only a very minute portion of iodide of amyl could be obtained. I recognised the hydrochlorate at once by its peculiar fatty appearance; and the platinum-salt crystallised in superb scales, exactly resembling the salt which I had often had occasion to prepare by the ordinary processes.

The following numbers were obtained on analyses:—

I.—0·2135 gramme of platinum-salt of amylamine gave 0·0715 gramme of platinum.

II.—0·2004 gramme of platinum-salt of amylamine gave 0·0682 gramme of platinum.

Or, in per centages:—

Experiment.		Mean.	Theory.
I.	II.		
33·48	34·13	33·76	33·76

Platinum-salt of Œnanthylamine.

I have already shown the presence of œnanthylene in Boghead naphtha.* The quantity of iodide of œnanthyl formed, appears to be exceedingly small, and I was only able to obtain enough platinum-salt for one determination. It consisted of beautiful orange-coloured scales.

0·1186 gramme of platinum-salt of œnanthylamine gave 0·0366 gramme of platinum.

Experiment.	Theory.
30·86	30·79

Platinum-salt of Caprylamine.

The iodide of capryl appears to be formed more readily than its congeners. The crystals of the platinum-salt of the corresponding base consisted of beautiful golden scales, some of them a quarter of an inch in diameter. They were soluble in alcohol and ether; the salt was, therefore, washed with a little water and pressed between folds of filtering-paper. Several grammes were prepared with comparative ease.

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* Philosophical Transactions, 1858.

The following numbers were obtained on analysis:—

I.—0·3432 grm. of platinum-salt of caprylamine gave 0·3616 grm. of carbonic acid, and 0·1906 grm. of water.
II.—0·2195 grm. of platinum-salt of caprylamine gave 0·0645 grm. of platinum
III.—0·2084 „ „ 0·0614 „
IV.—0·2028 „ „ 0·0596 „
V.—0·2066 „ „ 0·0616 „

	I.	II.	III.	IV.	V.	Mean.	Calculation.		
Carbon	28·73					28·73	C^{16}	96	28·62
Hydrogen	6·17					6·17	H^{20}	20	5·96
Nitrogen	. . .					. . .	N	14	4·17
Chlorine	. . .					. . .	Cl^3	106·5	31·74
Platinum	. . .	29·38	29·46	29·39	29·81	29·51	Pt	99	29·51
								335·5	100·00

The first and fourth analyses were made on the same specimen; the second, third, and fifth upon distinct preparations in each case.

Platinum-salt of Pelargonamine.

The iodide of pelargonyl was formed from Boghead naphtha in sufficient quantity to enable me to attain the hitherto unknown volatile alkaloid, pelargonamine. The crystals of the platinum-salt, although of a rich golden-yellow, were less beautiful than the others, and on drying at 100° C. caked slightly together. They did not, however, become in the least discoloured. The annexed numbers give the results of the analyses—

I.—0·3978 grm. of platinum-salt of pelargonamine gave 0·4474 grm. of carbonic acid, and 0·2304 grm. of water.
II.—0·1184 grm. of platinum-salt of pelargonamine gave 0·0340 grm. of platinum
III.—0·2132 „ , 0·0604 „
IV.—0·2364 „ „ 0 0678 „

	I.	II.	III.	IV.	Mean.	Calculation.		
Carbon	30·70				30·70	C^{18}	108	30·90
Hydrogen	6·44				6·44	H^{22}	22	6·30
Nitrogen	. . .				. . .	N	14	4·01
Chlorine	. . .				. . .	Cl^{3}	106·5	30·47
Platinum	. . .	28·71	28·33	28·68	28·57	Pt	99	28·32
							349·5	100·00

Each platinum-determination was made on a different specimen. I hope, eventually, to submit to the Society several more substances obtained from Boghead naphtha by the agency of hydriodic acid. It is evident that several of the true radicles may now be prepared by acting on the above iodides with sodium.

XLVI.—*On a New Series of Organic Compounds containing Boron.*

By Dr. E. Frankland, F.R.S.

[From the Philosophical Transactions for 1862.]

(Abstract.)

The substitution of a compound organic radicle for an elementary constituent in inorganic compounds has proved itself to be one of the most important and fertile fields of modern chemical investigation. The application of this species of substitution to the inorganic compounds of metals has called into existence an entirely new and extensive family of organic substances—the organometallic compounds—bodies never met with in nature, distinguished by well-marked affinities, and capable in some instances of effecting, in their turn, numerous substitutions of a like character. The realization of a similar substitution in the case of certain inorganic compounds of nitrogen and phosphorus, has, in the hands of Hofmann, not only enriched the science with a host of new and interesting compounds, but has also brought our knowledge of the organic bases to a degree of completeness, which cannot be rivalled in any other class of organic compounds. Lastly, attempts have not been wanting to extend these reactions to the oxygen-compounds of the metalloids; and although this portion of the field presents difficulties of a somewhat more formidable character, yet these attempts have not unfrequently been attended with success. Thus nitric oxide has been transformed into dinitroethylic and dinitromethylic acids;* sulphurous anhydride into ethylodithionic and methylotrithionic acids;† and carbonic anhydride into propionic and acetic acids.‡

The last-named reaction, confirming, as it did, the view previously expressed by Kolbe and myself,§ that organic compounds in general are nothing more than substitutions of this nature effected in carbonic oxide, in carbonic acid, and possibly in other inorganic compounds of carbon, naturally awakened a desire to extend this inquiry to the oxygen-compounds of boron and silicon, which are usually regarded as possessing certain important analogies with carbonic anhydride. With this end in view, boracic ether was submitted to the action of zincethyl by Mr. Duppa and myself. We found that the whole of the oxygen in boracic acid became replaced by ethyl, and in a short communication to the Royal Society,|| we described some of the properties of the remarkable body, boric ethide, thus formed. In the further study of this substance, and the extension of the research to the homologous methyl-compound, I much regret having been deprived of the co-operation of my friend and fellow-labourer, who had rendered me such valuable assistance at the commencement of the investigation, but who was reluctantly compelled to abandon its further prosecution.

The first attempt to replace oxygen by ethyl in boracic anhydride was made by exposing the latter in a finely pulverized condition to the action of zincethyl at various temperatures, but it was found that the zincethyl was utterly powerless to effect the desired substitution; neither did the anhydrous acid yield in the slightest degree to Wanklyn's compound of sodiumethyl and zincethyl, although it was digested and heated with it for several days. There could scarcely be a doubt that the intractability of

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* Philosophical Transactions for 1857, p. 59.

† Journal of Chemical Society, vol. x, p. 55, and p. 243.

‡ Ibid. vol. xi, p. 103; and Proceedings of the Royal Society, vol. x, p. 4.

§ Ann. Ch. Pharm. ci, 257. Proceedings of the Royal Institution of Great Britain for 1858.

|| Proceedings of the Royal Society, vol. x, p. 568.

the anhydride was due in great measure to its total insolubility in the surrounding liquid, and therefore, in order to place it under conditions more favourable for the action of the organo-metallic body, it was converted into boracic ether.

The ether was prepared by Rose's process,* which consists in distilling an intimate mixture of sulphovinate of potash and dried borax. The best proportions were found to be two parts by weight of borax, and three parts of the sulphovinate; but the yield of ether was very small, the greater part of the product consisting of alcohol. The removal of the latter by rectification, as recommended by Rose, involved the loss of much ether; recourse was therefore had to chloride of calcium for its abstraction, a method which gave very satisfactory results, the product of pure ether being more than doubled. The following is a sketch of the process finally adopted:—About 3 lbs. of the mixed borax and sulphovinate of potash were put into an ordinary Papin's digester, which was placed in a sand-bath and exposed to a very gradually increasing heat so long as volatile products came over. The crude distillate obtained from several such operations was then treated with about one-fourth of its weight of fused chloride of calcium, and agitated until the latter was dissolved. The liquid now separated into two layers, a lower one consisting of an alcoholic solution of chloride of calcium, and an upper one containing nearly all the boracic ether, which retained only a small proportion of alcohol in solution. The upper layer was decanted and submitted to distillation. It began to boil at about 85° C., but the thermometer soon rose to 118° C., between which temperature and 125° C. the greater part of the remaining liquid passed over and was reserved for the purposes of the investigation. A thick oily liquid remained in the retort, and appeared to consist of boracic acid united with a smaller proportion of oxide of ethyl.

On adding zincethyl to the boracic ether thus prepared, a considerable elevation of temperature gradually occurred, whilst at the same time a most penetrating and peculiar odour was developed, due apparently to the vapour of some volatile body, which not unfrequently burst into flame when the cork was removed from the flask in which the reaction took place. Some preliminary experiments showed that this volatile body could be distilled unchanged from the mixture, and that it was neither miscible with, nor apparently decomposed by, water. It was also spontaneously inflammable, and the beautiful green flame with which it burnt demonstrated the presence of boron as one of its constituents.

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* Pogg. Ann. xcviii, 245.

In order to prepare this body in sufficient quantity, several ounces of boracic ether were placed in a capacious flask closed by a doubly perforated cork. Through one of these perforations passed a thermometer, and through the other a short glass tube, one-fourth of an inch in diameter, and open at both ends: the bulb of the thermometer dipped into the boracic ether. Successive quantities of pure zincethyl were introduced through the short glass tube by means of a pipette, the elevation of temperature after each addition being allowed to subside before the next portion was added. The failure of a further addition of zincethyl to produce any rise of temperature was regarded as evidence of the completion of the reaction, which was not attained until a comparatively very large amount of zincethyl had been added.

The liquid in the flask was now submitted to distillation in an oil-bath. It began to boil at 94° C., and between this temperature and 140° C., a considerable quantity of a colourless liquid distilled over. The distillation then suddenly stopped, and, to avoid secondary products of decomposition by the application of a greater heat, the operation was interrupted. On cooling, the materials remaining in the flask solidified to a mass of large crystals of ethylate of zinc and zincethyl. On rectification, the distillate began to boil at 70° C., but the thermometer rapidly rose to 95°, at which temperature the last two-thirds of the liquid passed over and were received apart. The product thus collected exhibited a constant boiling-point on re-distillation.

The combustion with oxide of copper of this liquid and the remaining boron-compounds described in this paper, presented some difficulties, owing partly to the volatility of boracic acid in aqueous vapour, and partly to the tendency of that acid when fused, to encase particles of carbon and prevent their oxidation. Fortunately the errors thus introduced were not so considerable as to throw any doubts upon the analytical results, although in many cases the excess in the percentage of hydrogen and the deficiency in that of carbon are somewhat greater than usual. To estimate the boron in the liquid obtained as above described, advantage was taken of the complete decomposition of the compound when heated to 100° with concentrated nitric acid in sealed tubes. The whole of the boron was in this way converted into boracic acid; but the latter could not be determined by the direct evaporation of the nitric acid solution, the loss of boracic acid amounting in such an operation to 15 or 20 per cent. of the whole amount. None of the known processes for estimating this acid appeared to be eligible in the present instance, and it therefore became necessary to seek for a new one. After the trial of various methods with but indifferent success, it was found that the evaporation of the acid solution of boracic acid with a known weight of magnesia in excess, the residue being then ignited, presented a process which, although far from rigidly accurate, could not, in the case of the boron-compound to be analysed, diminish the amount of boron to a greater extent than about 0·2 per cent.

The analytical numbers agree with the formula

$$B\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5,\end{matrix}\right.$$

as shown by the following table:—

	Calculated.		Mean of analyses.
C_{12} . .	72	73·55	73·15
H_{15} . .	15	15·42	15·61
B . .	10·9	11·03	11·08
	97·9	100·00	99·84

The new body may be conveniently termed *boric ethide*. It is evidently formed by the replacement of the three atoms of oxygen in boracic acid by three atoms of ethyl, according to the following equation:—

$$2\underbrace{B\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{matrix}\right.}_{\text{Boracic ether.}} + 3\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zincethyl.}} = 2\underbrace{B\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Boric ethide.}} + 6\underbrace{\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2}_{\text{Ethylate of zinc.}}.$$

The ethylate of zinc thus produced combines with zincethyl to form the crystalline compound above alluded to. Hence the very large amount of zincethyl which was found necessary to complete the reaction.

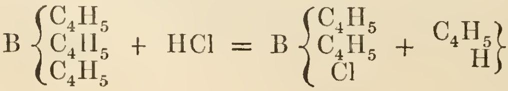
Boric ethide possesses the following properties:—It is a colourless mobile liquid of a pungent odour; its vapour is very irritating to the mucous membrane, and provokes a copious flow of tears. The specific gravity of boric ethide at 23° C. is 0·6961; it boils at 95° C. A determination of the specific gravity of its vapour by Gay-Lussac's method, gave the number 3·4006, which agrees very closely with that calculated upon the supposition that boric ethide is volumetrically composed like terchloride of boron, as is seen from the following calculation:—

1 vol. Boron vapour	·75319
3 vols. Ethyl	6·0117
The 4 vols. condensed to 2 vols. .	2)6·76489
	3·38244

The density of boric ethide vapour increases considerably as the temperature approaches the boiling-point; thus a determination made at 132° gave the number 3·5979, whilst a second showed the specific gravity of the vapour at 101°·6 to be no less than 3·757.

Boric ethide is insoluble in water, and is very slowly decomposed by prolonged contact with it. Iodine has scarcely any action upon it even at 100° C. It floats upon concentrated nitric acid for several minutes without change; but suddenly a violent reaction takes place, and crystals of boracic acid separate. When boric ethide vapour comes in contact with air, it produces slight bluish-white fumes, which in the dark are seen to proceed from a lambent blue flame. The liquid is spontaneously inflammable in air, burning with a beautiful green and somewhat fuliginous flame. In contact with pure oxygen it explodes. Excluded from the air, boric ethide is quite a stable body; a quantity of it kept in a sealed tube for two years exhibited, on examination, no evidence of any alteration.

When boric ethide is heated to 99° C. with strong hydrochloric acid over mercury, a considerable quantity of hydride of ethyl is slowly evolved, the reaction being



$$B\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\end{cases} + HCl = B\begin{cases}C_4H_5\\C_4H_5\\Cl\end{cases} + \left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}$$

When boric ethide is heated with water to 99° C. for several hours, it also appears to suffer an analogous decomposition, although with extreme slowness; even with hydrochloric acid, the action is so tedious, that I have not been able to prepare a sufficient quantity of boric chlorodiethide ($B(C_4H_5)_2Cl$) to examine its properties. In the cold, a strong solution of hydrofluoric acid has no action upon boric ethide, which also suffers scarcely any change by being heated to 99° C. for four hours with concentrated sulphuric acid. Gently heated for fourteen days with sodium in a sealed tube, boric ethide underwent no visible change.

Ammonia-Boric Ethide.

If a few drops of boric ethide be passed up into a dry eudiometer filled with mercury, and dry ammoniacal gas be then admitted into the same tube, each bubble of gas collapses with a shock, like that produced by a bubble of steam projected into cold water. A large quantity of ammonia is thus absorbed by boric ethide with extreme energy. To prepare the compound thus formed in larger quantity, several grammes of boric ethide were placed in a small flask filled with nitrogen and surrounded with ice: a current of dry ammoniacal gas was now passed into the flask as long as it was absorbed; finally, the product thus obtained was warmed to expel excess of ammonia, and then exposed *in vacuo* over sulphuric acid for twenty-four hours. It did not crystallize, and and could not be distilled, except *in vacuo,* without decomposition. Submitted to analysis, it yielded 61·43 per cent. of carbon and 15·43 per cent. of hydrogen. The formula

$$NH_3.B(C_4H_5)_3$$

requires 62·66 per cent. of carbon and 15·66 per cent. of hydrogen. The unavoidable slight oxidation of the boric ethide during the necessary manipulations affords a sufficient explanation of the deficiency in the amounts of carbon and hydrogen exhibited by the analysis. I should, however, have made renewed attempts to obtain this body in a state of greater purity, had not the investigation of the corresponding crystalline methyl-compound described below, left no doubt that the formula above given expresses the composition of ammonia-boric ethide.

Ammonia-boric ethide is a somewhat oily liquid, possessing an aromatic odour and an alkaline reaction. Carbonic acid has no action upon it, even in presence of water, but other acids decompose it instantly and liberate boric ethide. When it is exposed to a measured quantity of atmospheric air, there is scarcely any perceptible absorption of oxygen, even after the lapse of several hours.

Boric Dioxyethide.

When boric ethide is placed in a flask and allowed to oxidise gradually, first in dry air and finally in dry oxygen, it forms a colourless liquid, which boils at 125° C., but cannot be distilled under atmospheric pressure without partial decomposition. At the ordinary temperature, this product of oxidation evaporates without residue in a stream of dry carbonic acid. It can be distilled *in vacuo* without decomposition, and a portion so rectified yielded on analysis results agreeing with the formula

$$B(C_4H_5)_3O_4.$$

I regard this liquid as a compound of vinic ether, with a body having the formula

$$B\left\{\begin{matrix}C_4H_5\\O\\O\end{matrix}\right.$$

and derived from boracic acid by the substitution of one equivalent of ethyl for one of oxygen. For this body the name *boric dioxyethide* is appropriate, whilst its ethereal compound may be conveniently termed diethylate of boric dioxyethide. The formula of the latter will therefore be

$$B\left\{\begin{matrix}C_4H_5\\O\\O\end{matrix}\right. + \left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2, \text{ or } B\left\{\begin{matrix}C_4H_5\\C_4H_5O_2\\C_4H_5O_2.\end{matrix}\right.$$

The formation of diethylate of boric dioxyethide from boric ethide may be thus represented :—

$$B\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right. + O_4 = B\left\{\begin{matrix}C_4H_5\\C_4H_5O_2\\C_4H_5O_2.\end{matrix}\right.$$

This view of the constitution and mode of formation of the oxidised product is supported by its behaviour with water; for when diethylate of boric dioxyethide is placed in contact with water, it is instantly decomposed, alcohol and *dihydrate of boric dioxyethide* being formed, according to the following equation :—

$$\underbrace{B\begin{cases}C_4H_5\\C_4H_5O_2\\C_4H_5O_2\end{cases}}_{\text{Diethylate of boric dioxyethide.}} + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O_2 = \underbrace{B\begin{cases}C_4H_5\\HO_2\\HO_2\end{cases}}_{\text{Dihydrate of boric dioxyethide.}} + 2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2.$$

Dihydrate of boric dioxyethide may be conveniently prepared in a state of purity by agitating its aqueous solution with ether, which dissolves the boric compound. The ethereal solution must then be decanted, and on evaporation at common temperatures in a stream of dry carbonic acid, the new compound is left behind as a white and very volatile crystalline mass. The latter was sublimed at a gentle heat in a current of dry carbonic acid, and was made to condense in weighed tubes for analysis.

Dihydrate of boric dioxyethide is a colourless, volatile, crystalline body, very soluble in water, alcohol, and ether. It possesses an agreeable ethereal odour, and a most intensely sweet taste. Exposed to the air, it evaporates at ordinary temperatures, undergoing at the same time partial decomposition, and invariably leaving a slight residue of boracic acid. It may be sublimed without change at about 40° C. in a current of dry carbonic acid, and then condenses in magnificent crystalline plates resembling naphthaline. It fuses at a gentle heat, and at a higher temperature boils with partial decomposition. Its vapour tastes intensely sweet.

Boric dioxyethide might be regarded as the anhydride of a bibasic acid : the diethylate of boric dioxyethide would then be the ether of this acid, whilst the volatile crystalline body just described would be the hydrated acid itself. The latter does in fact redden litmus paper, but in other respects its acid qualities are very obscure, and I have not been able to form definite salts with it. It therefore scarcely possesses a valid claim to a place amongst the acids.

Considering boric ethide to be formed by the substitution of the ethyl in zincethyl for the oxygen in boracic acid, Mr. Duppa and myself expressed the reaction as follows :—

$$\underbrace{2B\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_5\\C_4H_5O_2\end{matrix}\right.}_{\text{Boracic ether.}} + \underbrace{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zincethyl.}} = \underbrace{2B\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Boric ethide.}} + \underbrace{6\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2}_{\text{Ethylate of zinc.}}.$$

Another, but less probable, view of the change presents itself in the supposition that the three atoms of ethyl in boric ethide were already present in the boracic ether, the action of the zincethyl being simply to remove the whole of the oxygen from the boracic ether. Kekulé* has in fact adopted this latter view of the reaction.

So long as the organic radicle of the zinc-compound and that of the boracic ether are identical, it is impossible to prove whether the three individual atoms of ethyl in boric ethide were originally present in the boracic ether, or have been derived from the zincethyl. Indicating by an asterisk the atoms of ethyl which finally become part of the boric ethide, it is impossible to prove conclusively whether the reaction takes place according to the first or the second of the following equations:—

$$(1)\quad 2B\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{matrix}\right. + 3Zn_2\left\{\begin{matrix}C_4H_5{*}\\C_4H_5{*}\end{matrix}\right. = 2B\left\{\begin{matrix}C_4H_5{*}\\C_4H_5{*}\\C_4H_5{*}\end{matrix}\right. + 6\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2.$$

$$(2)\quad 2B\left\{\begin{matrix}C_4H_5{*}O_2\\C_4H_5{*}O_2\\C_4H_5{*}O_2\end{matrix}\right. + 3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. = 2B\left\{\begin{matrix}C_4H_5{*}\\C_4H_5{*}\\C_4H_5{*}\end{matrix}\right. + 6\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2.$$

Although we cannot thus label, as it were, the atoms taking part in the reaction, we can unerringly trace the movements of the alcohol-radicles, if we secure their identification by varying their composition in the two compounds used in the process. The study of the action of zincmethyl upon boracic ether would obviously decide between these views. If boric ethide were produced from these materials, Kekule's hypothesis would be established; but if, on the other hand, boric methide were the result of the reaction, then the correctness of the view originally taken by Mr. Duppa and myself would be proved to be correct. The following are the results obtained in pursuing this inquiry:

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* Lehrbuch der org. Chemie, p. 489.

Boric Methide.

When a strong ethereal solution of zincmethyl is added to boracic ether, an elevation of temperature to the extent of 8° or 10° C. is observed, whilst at the same time a most intensely pungent odour is developed; this odour, although it resembles that of boric ethide, is far more powerful, and more persistently irritating to the mucous membrane. A slow evolution of a spontaneously inflammable gas, burning with a splendid green flame, was also noticed; and this evolution of gas became more rapid when the warmth of the hand was applied to the flask containing the ingredients. Preliminary experiments proved that this gas was nearly insoluble in water, but almost completely soluble in alcohol, the residue remaining undissolved being marsh-gas derived from the action of the alcohol upon traces of zincmethyl vapour with which the gas was contaminated. The gas was not condensed by a freezing mixture of ice and salt. It was, with the exception of a small percentage of marsh-gas, instantaneously dissolved by solution of ammonia, which yielded the gas again unchanged when neutralized by an acid. Concentrated sulphuric acid was without action upon the gas.

These data led to the following plan for collecting the gas in a state of purity. About two ounces of boracic ether were mixed in a small flask with rather more than their own bulk of an ethereal solution of zincmethyl, of such strength as to be spontaneously inflammable in a high degree. The flask, loosely corked, was placed in ice-cold water, and allowed to stand for a couple of hours until the reaction was complete: it was then furnished with a bent tube passing through a cork, and designed to conduct the gas into a second flask placed in a freezing mixture of ice and salt; from this flask the gas passed into a third containing about half an ounce of strong solution of ammonia. The air in the whole of the apparatus was now displaced by nitrogen, and the flask containing the boracic ether and zincmethyl removed from the ice-cold water. A slow evolution of gas immediately commenced, and was kept up at a convenient speed by plunging the generating flask into cold water, to which heat was very slowly applied. The gas, in passing through the freezing mixture, deposited nearly the whole of the ether and zincmethyl vapour with which it was contaminated; and on reaching the solution of ammonia, the boron-compound was instantaneously absorbed, whilst other gases, if present, passed through the ammonia unacted upon, and escaped into the atmosphere. The solution of ammonia soon became covered with a stratum of a lighter liquid, which increased in quantity until the stream of gas ceased to pass through. The ammonia-flask was now disconnected with the rest of the apparatus, and reserved for the next operation. The residue in the generating flask solidified to a crystalline mass on cooling.

It now only remained to disengage the gaseous boron-compound from its combination with ammonia. For this purpose the ammonia-flask was fitted with a funnel-tube terminating beneath the surface of the liquid, and a gas-delivery tube, the latter leading to a Liebig's potash-apparatus charged with concentrated sulphuric acid; finally, the opposite extremity of the latter apparatus was connected with a mercurial gas-holder. To prevent dangerous explosions, on the elimination of the spontaneously inflammable gas from its ammonia-compound, the whole of the air-spaces of the apparatus were filled with nitrogen. Everything being thus prepared, dilute sulphuric acid was gradually poured into the ammonia-flask through the funnel-tube, the contents of the flask being frequently agitated. No gas was evolved until the excess of ammonia was saturated; then, however, it was given off abundantly, and the addition of a few drops of dilute sulphuric acid, from time to time, through the funnel-tube, served to keep up a convenient current. The gas was allowed to pass freely through the depressed mercurial gas-holder until a sample of it proved, by its perfect solution in ammonia, that all nitrogen had been swept from the apparatus. The exit-tube of the gas-holder was now closed, and the gas collected in sufficient quantity for subsequent experiments.

The following determinations, together with the analysis of its ammonia-compound, prove that this gas is *boric methide*, and that its formula is

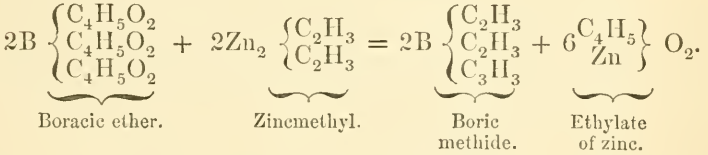
$$B \begin{cases} C_2H_3 \\ C_2H_3 \\ C_2H_3. \end{cases}$$

An indefinite quantity of the gas was cautiously led over ignited oxide of copper, the carbonic acid and water produced being collected and weighed in the ordinary manner. 0·5875 grm. of carbonic acid and 0·3664 grm. of water were obtained. These numbers show that the atomic relation of carbon to hydrogen is as 2 : 3.

A determination of the specific gravity of the gas gave the number 1·9108—coinciding closely with the calculated specific gravity of boric methide, which contains 1 volume of boron vapour and 3 volumes of methyl, the four volumes being condensed to two.

1 vol. boron vapour . . .	·75319
3 vols. methyl	3·10956
	2)3·86275
	1·93137

Boric methide is produced from boracic ether and zincmethyl by the following reaction :—



$$\underbrace{2B\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{matrix}\right.}_{\text{Boracic ether.}} + \underbrace{2Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zincmethyl.}} = \underbrace{2B\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_3H_3\end{matrix}\right.}_{\text{Boric methide.}} + \underbrace{6\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}}_{\text{Ethylate of zinc.}} O_2.$$

The formation of boric methide under these circumstances proves conclusively that the corresponding ethyl-compound is formed, not by the removal of the whole of the oxygen from boracic ether, but by the actual substitution of the three atoms of oxygen in boracic acid by three atoms of ethyl, whilst boric methide is in like manner produced by the similar substitution of methyl for oxygen,—a kind of substitution which is quite in harmony with the mode of formation of very numerous compounds in the organo-metallic family.

Boric methide exists at ordinary temperatures as a colourless and transparent gas, possessing a peculiar and intolerably pungent odour, irritating the mucous membrane, and provoking a copious flow of tears. Its specific gravity is 1·93137. It retains its gaseous condition when exposed to a cold of —16° C.; but at 10° C., and under a pressure of three atmospheres, it condenses to a colourless, transparent, and very mobile liquid. It is very sparingly soluble in water, but very soluble in alcohol and in ether. In contact with atmospheric air it takes fire spontaneously, burning with a bright green flame, which is very fuliginous if the volume of the flame be considerable. If the gas issue into the air through a tube $\frac{1}{10}$th of an inch in diameter, the amount of smoke is surprisingly great, two or three cubic inches of gas, when consumed in this way, filling the atmosphere of a capacious room with large comet-like flocks of carbonaceous matter. This curious phenomenon is probably due, in part at least, to the formation of a superficial coating of boracic acid, which envelopes the particles of carbon, and prevents their combustion. Suddenly mixed with atmospheric air or oxygen, boric methide explodes with great violence. In contact with air, both boric methide and the vapour of boric ethide exhibit two distinct kinds of spontaneous combustion. Thus, when these bodies issue very slowly from a glass tube into the air, they burn with a lambent blue flame invisible in daylight, and the temperature of which is so low that a finger may be held in it for some time without much inconvenience. Under these circumstances partial oxidation only takes place, and it is to the products thus formed that the peculiar pungent odour of boric ethide and boric methide is due. When, on the other hand, these bodies issue into the air more rapidly, the lambent blue and nearly cold flame changes to the green and hot flame above-mentioned. I have not examined the spectra of the two differently coloured flames from the same compound, but they doubtless present a widely different appearance, thus affording another instance of the dependence of the spectra of bodies upon temperature,—a phenomenon to which Dr. Tyndall and myself recently called attention in the case of lithium*.

Boric methide is not acted upon by binoxide of nitrogen or by iodine. Solution of bichromate of potash scarcely effects it, but the addition of concentrated sulphuric acid at once determines the reduction of the chromic acid. When boric methide is allowed to bubble through water into chlorine, each bubble burns explosively with a bright flash of light and the separation of carbon. It has no tendency to unite with acids. Concentrated sulphuric acid has no action upon it; when mixed with hydriodic acid gas, it suffers no change; but, on the other hand, it is freely absorbed by solutions of the fixed alkalies, and by ammonia. If a very rapid current of the gas, mixed with half its volume of marsh-gas, be passed through a stratum of strong solution of ammonia only half an inch deep, not a trace of boric methide escapes absorption.

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* Philosophical Magazine [4], xxii, 472.

Ammonia-Boric Methide.

When dry ammoniacal gas is mixed with an equal volume of dry boric methide, both gases instantly disappear, with evolution of a considerable amount of heat, and production of a white, volatile, crystalline compound. The latter is also formed when boric methide is passed into solution of ammonia. The colourless liquid stratum which forms upon the surface soon solidifies when it is placed over sulphuric acid *in vacuo*. A quantity of the compound obtained by this latter process was purified by solution in ether and subsequent recrystallisation. On being submitted to analysis, it yielded results agreeing with the formula—

$$NH_3 + B(C_2H_3)_3.$$

Ammonia-boric methide is deposited from its ethereal solution in magnificent arborescent crystals, which rapidly volatilize without residue when exposed to the air. They possess a caustic and bitter taste, and a very peculiar odour, in which both the smell of ammonia and of boric methide can be recognised. Ammonia-boric methide fuses at 56° C. and boils at about 110° C. In a current of air, or better, of carbonic acid, it sublimes at a very gentle heat, and condenses in magnificent arborescent crystals. Determinations of the specific gravity of its vapour, at three different temperatures, gave the numbers 1·251, 1·258, and 1·250, indicating that the vapour of ammonia-boric methide consists of equal volumes of boric methide and ammonia united without condensation :—

1 vol. Boric Methide . . .	1·93137
1 vol. Ammonia	·5873
	2)2·51867
	1·25933

Thus the formula of ammonia-boric methide is a four-volume formula,* a state of condensation which is usually considered to be abnormal, and which, when it occurs, is generally explained by the assumption of a decomposition of the body at the moment of conversion into vapour. The proof of the disunion or integrity of the vaporous molecule of ammonia-boric methide would be interesting in connexion with these so-called anomalous vapour-densities, but I have to regret my inability to offer any sufficiently decisive solution of this problem. The difficulty to be overcome is the finding of a reagent that will not decompose ammonia-boric methide at elevated temperatures, but which would absorb ammonia only, out of a mixture of this gas with boric methide, at a temperature above the boiling-point of ammonia-boric methide. Chloride of calcium does not decompose ammonia-boric methide; but although it readily absorbs ammonia at ordinary temperatures, it allows the whole of it to escape at 110° C. Chloride of zinc decomposes ammonia-boric methide before the latter volatilizes. The same effect is produced by all the strong acids, which are therefore also inadmissible, whilst dry boracic acid does not absorb ammonia even at ordinary temperatures. The substance which appeared to be best adapted for this reaction was dry and recently fused chloride of copper. This salt does not decompose ammonia-boric methide below the boiling point of the latter, whilst it readily absorbs ammonia, and retains it at a temperature of 160° C. I will now describe the mode in which an experiment with this substance was conducted, and the results which were obtained. A quantity of ammonia-boric methide was introduced into a graduated tube filled with mercury, and inverted in a vessel containing the same metal. The whole was now immersed in an oil-bath, and heat applied until the boron-compound was converted into vapour, the volume of which, at a known temperature and pressure, was then observed. After the apparatus had been allowed to cool, a fragment of chloride of copper was passed up into the tube, and heat again applied. The boron-compound soon melted and enveloped the fragment of chloride of copper: as the temperature approached the boiling-point of ammonia-boric methide, the latter slowly boiled off from the chloride of copper, and the vapour then occupied the same volume as that read off before the introduction of the chloride of copper. The mercury in the tube remained steady for two or three minutes; it then gradually ascended, and the contraction of the vapour-volume continued until it was reduced to exactly one-half, as indicated by the following numbers:—

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* $H_2O_2 = 2$ vols.

Corrected volume of vapour before treatment with chloride of copper . .	35·67 cub. centims.
Ditto after treatment with chloride of copper	17·85 cub. centims.

By treatment with chloride of copper, 100 volumes of vapour were therefore reduced to 50·04 vols., and the residue consisted of pure boric methide gas. It is obvious that this absorption may be due either to decomposition of the vapour of ammonia-boric methide *by chloride of copper* at an elevated temperature, or to the decomposition *by heat* of the boric compound into equal volumes of boric methide and ammonia, the latter being then absorbed by the chloride of copper. Unfortunately, the result of the experiment is not sufficiently decisive to compel the adoption of either of these hypotheses, although the formation of the vapour and its existence for a few minutes in contact with chloride of copper favour the first more than the second; thus indicating that the vapour of ammonia-boric methide consists of equal volumes of ammonia and boric methide united without condensation, a result which would harmonize with the very generally observed rule, that when two gases or vapours unite in equal volumes, the volume of the compound is equal to that of its constituents.

Ammonia-boric methide scarcely absorbs a perceptible amount of oxygen at ordinary temperatures, even after several days' exposure to the gas; but it takes fire below 100° C. when heated in contact with the air. Its vapour is also very inflammable; thus, when ammonia-boric methide is placed under the receiver of an air-pump, and the air is being withdrawn, the explosion of the mixture of air and vapour in the cylinders of the pump is frequently determined by the rise of temperature consequent upon the depression of the pistons when the rarefaction has become considerable.

Boric methide is also absorbed by aniline with great avidity. Acids expel the gas from this compound unchanged.

Terhydride of phosphorus has no action upon boric methide. A mixture of equal volumes of the two gases is spontaneously inflammable, burning with a yellowish-white flame, in which the characteristic green tinge attending the combustion of boric methide is no longer perceptible.

Compounds of Boric Methide with Potash, Soda, Lime, and

Baryta.—Solution of caustic potash absorbs boric methide with great energy. The saturated solution, exposed over sulphuric acid, *in vacuo,* dries down to a gummy mass, which scarcely exhibits signs of crystallisation. The same body may be more conveniently formed by decomposing ammonia-boric methide with alcoholic solution of potash, taking care to employ an excess of the former. On evaporation over sulphuric acid *in vacuo,* the excess of the ammonia-compound volatilizes, and is decomposed by the sulphuric acid, with elimination of boric methide: thus the potash-compound evaporates in an atmosphere of boric methide. Nevertheless even by this method I did not succeed in obtaining the potash-compound in a state of purity, potash-boric methide thus prepared yielding on analysis 47·93 per cent. of potash, and 42·86 per cent. of boric methide, numbers only very remotely indicating the formula

$$KO.B(C_2H_3)_3,$$

which requires 45·67 per cent. of potash and 54·33 per cent. of boric methide. The appearance of the compound, even after exposure to gentle heat *in vacuo,* suggested the presence of water, which could not, however, be expelled at a temperature below that at which potash-boric methide itself is decomposed.

Boric methide is also readily absorbed by solution of neutral carbonate of potash, bicarbonate of potash and potash-boric methide being apparently formed. Although boric methide and potash unite with remarkable energy, yet they are separated by acids with the greatest readiness; even carbonic acid in the presence of water can expel boric methide from its potash-compound; thus, if an aqueous solution of potash-boric methide be passed into carbonic acid standing over mercury, the acid gas soon becomes replaced by pure boric methide.

Soda-boric methide, baryta-boric methide, and *lime-boric methide* are similar bodies, produced by the absorption of boric methide gas by caustic solutions of soda, baryta, and lime; they are all readily soluble in water, and react alkaline.

Boric methide in combination with the alkalies and alkaline earths has almost entirely lost its powerful affinity for oxygen; nevertheless, when these bodies are placed in contact with a known quantity of oxygen over mercury for several days, the volume of the gas perceptibly diminishes.

The great difficulty, not to say danger, attending the gradual oxidation of considerable quantities of a gaseous and spontaneously inflammable body like boric methide, has prevented me from following this compound into its products of oxidation, as was done in the case of boric ethide. With a graduated supply of oxygen, however, boric methide appears to comport itself like boric ethide, and the compounds formed are probably homologous with diethylate and dihydrate of boric dioxyethide.

In conclusion, it can scarcely be doubted that the action upon boracic ether of the zinc-compounds of the remaining alcohol-radicles would produce the homologues of the bodies described in the foregoing pages. It may also be remarked, that the existence of bodies like boric dioxyethide, in which one-third of the oxygen in boracic anhydride is replaced by ethyl, altogether abolishes any supposed analogy between carbonic and boracic acids, whilst it proves that the composition of the latter acid is expressed by the formula BO_3, or some multiple of that formula. I am at present engaged in studying the action of zincethyl and sodium-ethyl upon the ethers of silicic, carbonic, oxalic, and acetic acids.

XLVII.—*On a Method for the Determination of Nitric and Nitrous Acids.*

By A. Vernon Harcourt, M.A., Student of Christ Church, Oxford.

In the course of some experiments upon the alkaline peroxides*, I had occasion to determine the quantity of nitrogen in a mixture of nitrate and nitrite of potassium. Finding no account of a method suitable for this purpose, I was compelled to seek one experimentally. That at which I arrived, and which is briefly indicated in the paper referred to, gives very exact results, and promises to be available for the determination of any nitrate or nitrite whatsoever and however admixed.

Since that time a method has been published by Professor

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* Journ. Chem. Soc., vol. 16, p. 289.

Schulze,[*] differing only in one important particular, the employment of platinized zinc in the place of zinc and iron, from that pursued by me. A brief account of this latter method, and its results, may, however, still be acceptable.

It has long been known, that when nitre is heated with an excess of potash, zinc, and water, ammonia gas is evolved. But the conversion effected in this way is incomplete. In a number of experiments made with the view of founding a quantitative method upon this reaction, the ammonia thus formed was collected and determined; it amounted to about $\frac{3}{4}$ths of that quantity, which the weight of nitre used was theoretically capable of yielding. No modification in the proportions of zinc and potash solution, or in the degree of concentration of the latter, materially improved this result. Under no conditions was the relation sufficiently constant to furnish an empirical number. Nitre, heated in a combustion-tube with a mixture of powdered zinc and soda-lime, yielded only a trace of ammonia.

It was observed, I believe, by Mr. Griffin,[†] that, when a moderately concentrated solution of potash is poured upon a mixture of zinc and iron, hydrogen is freely disengaged, even without the application of heat. This action is electrolytic; the zinc is oxidized, and the hydrogen formed upon the surface of the iron. A similar effect is observed if platinum, copper, or tin, be substituted for iron; but the action with these metals is less energetic. The addition of a nitrate to the mixture evolving hydrogen, is followed by an immediate development of ammonia. This reaction furnishes a good qualitative test of the presence of nitric or nitrous acid. The fluid to be examined is reduced to a small bulk, and poured into a test-tube containing two or three grammes of a mixture of granulated zinc and clean iron filings. A small quantity (5 or 6 c.c.) of strong potash solution is added, and the whole heated to boiling. The usual tests for ammonia may be applied at the mouth of the tube: ·005 grm. of nitre thus treated, gave a distinct reaction with reddened litmus paper. The employment of potassio-iodide of mercury renders this test far more delicate. The mixture should be gently boiled for five or ten minutes, and the evolved gases led into a small quantity of dilute hydrochloric acid. The acid solution is is supersaturated with potash, and tested with a drop of potassio-iodide of mercury: ·001, ·0005, and even ·0001 grms. of nitre gave a distinct red coloration when thus treated.

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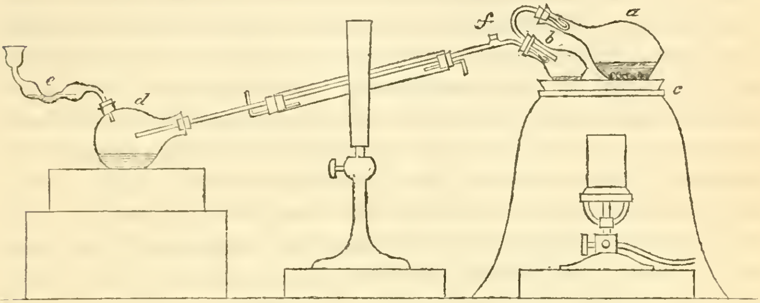
[*] Chem. Central Blatt, No. 53.

[†] Griffin's Chemical Recreations, p. 231.

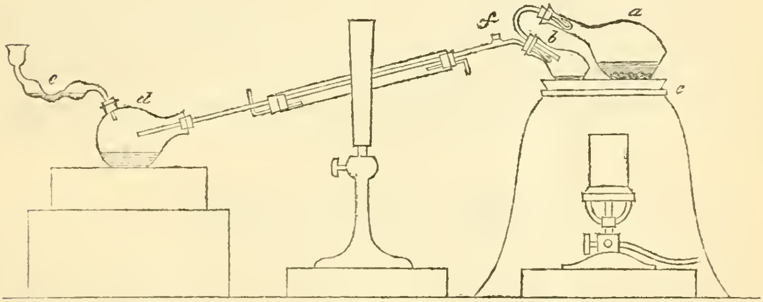
The apparatus which I have employed for quantitative determinations is represented, on a scale of $\frac{1}{8}$th, in the following figure.



The flask, *a*, which has a capacity of 200 C.C., is designed for the generation of ammonia by the mutual action of nitric acid, zinc, iron, potash, and water. It is connected by a bent tube, drawn out and recurved at its extremity, with the smaller flask or bulb *b*; and the two are so arranged, that they both rest at a considerable angle of inclination upon the sand-bath, *c*. The smaller flask is connected with a condenser which leads into the tubulated receiver, *d*. In the upper part of the condensing tube is a small tubulure *f*, closed during the distillation by a plug of india-rubber. The tube, *e*, which is provided with two or more bulbs and a funnel-head, has the shape indicated in the figure. It is fastened into the tubulure by means of a perforated plug of caoutchouc, which, when slightly greased, makes a tight and supple joint. A standard solution of sulphuric acid is used for the collection and determination of the ammonia. The excess of acid employed is finally determined by means of a standard solution of caustic potash.

The following is the course of the operation:—The funnel-tube, *e*, is brought into a vertical position, by being turned round in the tubulure through half a circle; a quantity of standard acid from a burette is passed through it into the receiver, more than enough to neutralize all the ammonia that can be formed. Some litmus solution is added to render visible the progress of the action. The funnel-tube is then restored to a horizontal position, and its bulbs filled up to the proper level by a few drops more of the standard acid. The total quantity of acid that has been taken, is now read off upon the burette. The flask *a* is then removed, its tube and cork, together with the smaller flask, which should contain a little water, remaining in position upon the sand-bath. Into it is introduced about 50 grms. of finely granulated zinc, together with half that quantity of iron filings, which have been cleansed by sifting, and ignition in a covered crucible; a weighed portion of the nitrate to be determined is then introduced, with water sufficient to dissolve it; lastly, a measured quantity of a solution of caustic potash, free from nitre, is added, and the flask immediately replaced. It is essential that the quantity of the metals and of the potash employed, should greatly exceed that proportion which is theoretically necessary for the complete conversion of the nitric acid. In my experiments with nitre, I have generally taken about 0·5 grm. of that substance, 20 c.c. of water, and 20 c.c. of a solution of potash, sp. gr. 1·3. Provided the quantity of potash be sufficient, it is immaterial in what degree its solution is diluted, since, in the course of the distillation, it passes through every stage of concentration. It must not be highly concentrated at the commencement of the operation.

Heat is now applied to the part of the sand-bath immediately beneath the larger flask, and the fluid is gradually raised to the boiling point. If the bubbles of air and hydrogen pass at a moderate rate through the bulb-tube, *e*, there is no risk of a loss of ammonia. When distillation has commenced, the lamp is so placed that the water in the smaller flask *b* may also boil gently. The fluid is thus twice distilled in one operation, and the traces of potash which escape from the flask *a*, are effectually retained in the flask *b*. The end of each of the two exit-tubes is drawn out, and bent into a hook for further security. Repeated experiment has proved the sufficiency of this arrangement for keeping back in a slow distillation everything that is not volatile. The quantity of fluid in the flask *b* can be regulated by adjusting the position of the lamp. The distillation, which should occupy from one to two hours, requires only occasional attention. It may be terminated when hydrogen gas, which is evolved in larger quantity as the potash becomes concentrated, has been passing regularly, for five or ten minutes, through the bulb-tube *e*. When the fluid in *e* has receded, as the apparatus cools, into the inner bulb, the caoutchouc plug is withdrawn from *f*, and a stream of water poured into the condensing tube, to preclude the possibility of ammonia being retained upon any portion of its surface. The tube *e* is then turned round into the vertical position, and water is passed through it two or three times, after which it is removed, and the tubulure of the receiver closed by a cork. Finally, the receiver itself is disconnected, the end of the condensing tube is rinsed externally, and the determination is completed by adding standard alkali from a burette to the fluid in the receiver till a change of colour appears. Collection in hydrochloric acid, and precipitation by choride of platinum, may be substituted, but the volumetric method gives perfectly sharp results.



The zinc and iron which remain in the generating flask need only to be washed with water, with dilute acid, and again with water, to be ready for a second determination. Metals that have once been used, generate hydrogen far less actively than zinc with a bright surface, and freshly ignited iron; but the production of ammonia proceeds as readily with one as with the other. It may be safely assumed, that the presence of any salts, which are without action upon caustic potash, or upon zinc and iron, will not interfere with the reaction upon which this method depends. The experiment was, however, made of mixing weighed quantities of nitre with various proportions of sulphate of potassium and chloride of sodium. The presence of these salts did not affect the result.

For the estimation of nitric acid in other than alkaline nitrates, the separation of the base may, in some cases, prove a necessary preliminary. I have experimented only with nitrate of barium and nitrate of lead. The former may be determined exactly in the same way as nitrate of potassium, and with equally good results. The carbonate of barium, which separates on adding solution of caustic potash, is, as might be expected, without influence on the reaction. Nitrate of lead exhibits a slight deficiency when thus directly determined. In five experiments, instead of 8·45 per cent. of nitrogen, the following numbers were found—7·78, 7·83, 8·09, 8·28, 8·11. This deficiency is possibly due to an action of dissolved oxide of lead upon the surface of the zinc. It would certainly disappear if the lead were first separated by means of sulphate of potassium.

A few examples of determinations made by this method are given in conclusion.

A solution of pure nitre was made, and of this 10 c.c. were used in each experiment. This quantity evaporated to dryness, left a residue weighing 0·3838 grm. 1 c.c. of the standard acid employed neutralizes an amount of ammonia, containing 0·002084 grm. of nitrogen. In six consecutive experiments, the number of c.c. of this acid required was—

(1). 25·7, (2). 25·3, (3). 25·3,
(4). 25·4, (4). 25·4, (6). 25·6,

of which the mean is 25·45 c.c.: hence the total nitrogen found is 0·05304 grm.; the nitrogen per cent. 13·82; theory requires 13·86.

In eight consecutive experiments, made with the same standard acid, the quantity of nitre taken for each was 0·4986 grm.

The number of cubic centimetres required was,—

(1). 33·15, (2). 32·9, (3). 33·1, (4). 33·2,
(5). 33·05, (6). 33·1, (7). 33·15, (8). 33·2,

of which the mean is 33·1: hence the total nitrogen found is 0·069; the nitrogen per cent. 13·83.

XLVIII.—*On Oxide of Ethylene, considered as a link between Organic and Mineral Chemistry.*

[A Discourse delivered to the Fellows of the Chemical Society of London, June 5th, 1862.]

By M. Ad. Wurtz.

In the year 1795, four Dutch Chemists, Deiman, Troostwyk, Bondt, and Lauwerenburgh, first made the remarkable experiment of bringing together equal volumes of chlorine and olefiant gases, whereby they obtained a liquid compound, still known by the name of "Dutch liquid." This compound is an organic chloride, the dichloride of the diatomic radicle, olefiant gas or ethylene; and its constitution, or rather its mode of formation and most of its chemical properties, show that it may be represented by the formula

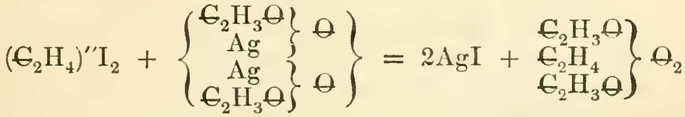
$$(C_2H_4)''Cl_2$$

Oxyde of ethylene is the corresponding oxide—

$$(C_2H_4)''O$$

This oxide cannot be formed directly by the action of oxygen on ethylene,* but it is obtained as a derivative of glycol, of which it is the anhydride or ether.

I must here draw attention to the re-actions by which glycol is produced, for they exhibit a remarkable peculiarity, on which I must especially insist. I obtained this body by the action of potash or baryta on diacetic glycol, a compound produced by the action of bromide or iodide of ethylene on acetate of silver, as shown by the following equation:—



$$(C_2H_4)''I_2 + \left\{ \begin{array}{c} \left.\begin{array}{c} C_2H_3O \\ Ag \end{array}\right\} O \\ \left.\begin{array}{c} Ag \\ C_2H_3O \end{array}\right\} O \end{array} \right\} = 2AgI + \left.\begin{array}{c} C_2H_3O \\ C_2H_4 \\ C_2H_3O \end{array}\right\} O_2$$

Here we see clearly that 2 atoms of silver are removed, and their place supplied by ethylene, which, thus, as it were, rivets together the residues of the two molecules of acetate, producing diacetic glycol. Polyatomic radicles are indeed especially characterised by the power which they possess of partially encroaching on several molecules belonging to a simple type, and thus joining these molecules together, so as to form a more complex type. Glycol itself, for example, may be supposed to result from the substitution of ethylene for 2 atoms of hydrogen in two molecules of water thus rivetted together:—

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* I have in vain endeavoured to bring about the direct combination of oxygen and ethylene, by heating a mixture of the two gases in the required proportions in a sealed flask containing acetic acid. I hoped to obtain by this method the acetate of ethylene or acetic glycol.

$$\left.\begin{array}{c}\mathrm{H}\\ \mathrm{H_2}\\ \mathrm{H}\end{array}\right\}\mathrm{Ɵ_2} \qquad\qquad \left.\begin{array}{c}\mathrm{H}\\ \mathrm{(Ꞓ_2H_4)''}\\ \mathrm{H}\end{array}\right\}\mathrm{Ɵ_2}$$

I must not omit to notice here that the general idea just enunciated was first suggested by Professor Williamson,* when he represented sulphuric acid as derived from two molecules of water in which two atoms of hydrogen are replaced by the radicle sulphuryl:

$$\left.\begin{array}{c}\mathrm{H}\\ \mathrm{H_2}\\ \mathrm{H}\end{array}\right\}\mathrm{Ɵ_2} \qquad\qquad \left.\begin{array}{c}\mathrm{H}\\ \mathrm{S̶Ɵ_2}\\ \mathrm{H}\end{array}\right\}\mathrm{Ɵ_2};$$

but I believe myself justified in adding that my own researches on the glycols have afforded a tangible representation, and, as it were, an experimental demonstration of this idea, and have served to establish the notion of polyatomic radicles in organic chemistry.

Glycol cannot be dehydrated directly so as to transform it into oxide of ethylene. This transformation is however effected indirectly, by first subjecting glycol to the action of chlorhydric acid, which expels the water and forms chlorhydric glycol, and by then treating this body with caustic potash—

$$\mathrm{Ꞓ_2H_4Ɵ.H_2Ɵ} + \mathrm{HCl} = \mathrm{Ꞓ_2H_4Ɵ.HCl} + \mathrm{H_2Ɵ}$$
$$\mathrm{Ꞓ_2H_4Ɵ.HCl} + \mathrm{KHƟ} = \mathrm{Ꞓ_2H_4Ɵ} + \mathrm{H_2Ɵ} + \mathrm{KCl}$$

On adding caustic potash to chlorhydric glycol or chlorhydrate of oxide of ethylene, an immediate precipitation of chloride of potassium takes place, accompanied by violent evolution of gas. This gas conducted into a cooled receiver, condenses into a light, transparent mobile liquid, which is oxide of ethylene.

This compound boils at 13·5°. It is miscible in all proportions with water and with alcohol. Like the isomeric body aldehyde, it reduces nitrate of silver, but more slowly.

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* Chem. Soc. Qu. J. iv., 350.

Oxide of ethylene is a very plastic compound, which is capable of uniting directly with a host of bodies: with hydrogen to form alcohol; with oxygen to form glycolic acid; with bromine, forming red crystals, consisting of a bromide of oxide of ethylene, having the composition $2\text{Ȼ}_2\text{H}_4\text{Ꝋ},\text{Br.}^2$; with water, to form glycol, and the polyethylenic alcohols; and, lastly, with ammonia, to form oxygenated bases.

These properties taken together show that oxide of ethylene is analogous to certain oxides belonging to the domain of mineral chemistry. To bring out this analogy by the comparison of its constitution and re-actions with those of the mineral oxides in question, is the object of the present lecture.

In the first place, the basic properties of oxide of ethylene may be demonstrated by a very striking experiment. If a concentrated solution of chloride of magnesium be introduced into a flask, together with oxide of ethylene, the flask then sealed, and the whole left to itself for about 24 hours, an abundant deposit of hydrate of magnesia is produced, while chlorhydric glycol (chlorhydrate of oxide of ethylene) remains in solution. The oxide of ethylene has, consequently, displaced the magnesia; and, in like manner, it displaces alumina, ferric oxide, and cupric oxide. It behaves, therefore, like an oxide, and accordingly we represent it as an oxide, expressing its composition by the formula

$$(\text{Ȼ}_2\text{H}_4)''\text{Ꝋ},$$

in which the ethylene plays the part of a diatomic radicle.

The question now arises: Do radicles of this nature exist among the metals, and are there any metallic oxides which can be compared, as to their constitution, with oxide of ethylene?

With the view of obtaining an answer to this question, we shall compare with oxide of ethylene, the oxides of *barium, strontium, calcium, magnesium, manganosum, ferrosum, zinc, copper, lead, mercury, &c.*, representing them by the formulæ

$$\cancel{\text{Ba}}''\text{Ꝋ},\ \cancel{\text{Sr}}''\text{Ꝋ},\ \text{Ȼa}''\text{Ꝋ},\ \cancel{\text{Mg}}''\text{Ꝋ},\ \cancel{\text{Mn}}''\text{Ꝋ},\ \cancel{\text{Fe}}''\text{Ꝋ},\ \cancel{\text{Zn}}''\text{Ꝋ},\ \cancel{\text{Pb}}''\text{Ꝋ},\ \cancel{\text{Hg}}''\text{Ꝋ}.$$

In these formulæ, the metals are regarded as diatomic, and, as possessing atomic weights double of those which are commonly assigned to them, thus becoming analogous to ethylene, so far as regards their combining capacity. But are we justified in doubling the atomic weights of these metals? We shall endeavour to show that this view is supported by facts, relying in the first place, on certain physical proofs, and afterwards adducing a certain number of arguments, drawn from chemistry itself, in favour of the opinion that we have adopted. It is right to add that the notion of polyatomic metals was introduced into chemical science by Dr. Odling, and that the idea of regarding the metals abovementioned as diatomic, and doubling their atomic weights, was first conceived by M. Cannizzaro.

Observe, in the first place, that the atomic weights in question are the same as those of Berzelius. This will be seen from the following table:—

Names of the Elements.	Berzelian Atomic Weights.		Gerhardt's Atomic Weights.	New Atomic Weights.
	Referred to 100 of Oxygen.	Referred to 1 of Hydrogen.		
Hydrogen	6·25	1	1	1
Oxygen	100	16	16	16
Sulphur	201·16	32·2	32	32
Chlorine	221·3	35·5	35·5	35·5
Bromine	499·8	79·8	80	80
Iodine	792·99	126·8	127	127
Nitrogen	88·5	14·1	14	14
Phosphorus	196	31·5	31	31
Arsenic	469·4	75·1	75	75
Carbon	75·12	12	12	12
Silicium	277·7	{ 44·4, $\frac{2}{3}$ of which = 28 }	28	28
Tin	735·29	117·6	58·75	118
Barium	855·29	136·8	68	136·8
Strontium	545·9	87·3	43·8	87·3
Calcium	251·65	40·2	20	40
Magnesium	158·14	25	12	24
Manganese	344·6	55·1	27·8	55·6
Iron	350·5	56·1	28	56
Zinc	406·59	65	32·5	65
Cadmium	696·77	111·4	55·7	111·4
Copper	395·6	63·3	31·5	63
Lead	1294·6	207	103·5	207
Mercury	1251·29	200·2	100	200
Silver	1351·6	215·6	108	108
Potassium	489·9	78·3	39	39
Sodium	290·9	46·5	23	23
Lithium	81·66	13	6·5	6·5

It will be seen that the atomic weights in the second column are, for a considerable number of metals, double of those proposed by Gerhardt. It is these double atomic weights that are represented by the barred symbols of the preceding formulæ, which, in fact, are identical with the old formulæ of Berzelius:* for the bars, which are, perhaps, necessary during the existing confusion of symbols, are merely provisional and will ultimately fall into disuse.

These double atomic weights are applicable to the diatomic metals above-mentioned, but not to *silver, potassium, sodium,* and *lithium,* which are monatomic and comparable with hydrogen. With regard then to the metals included in the preceding table, we adopt the atomic weights of Berzelius, excepting for the last four metals, which retain the smaller atomic weights adopted by Gerhardt.

The new system of atomic weights accords better than any other, with the physical data which serve to control the determination of the relative weights of the atoms. In fact, the numbers in the last column are identical with those designated by M. Regnault as "thermic equivalents." This philosopher has observed that the law of Dulong and Petit, according to which, the specific heats of the elementary bodies are to one another in the inverse ratio of their atomic weights, presents but few exceptions; and that even these disappear if we admit for hydrogen, potassium, sodium, and silver equivalents half as great as those generally adopted,—that is to say, if, while we retain the usual equivalents of the other elements, we assign to the four bodies just mentioned, the numbers $\frac{1}{2}$, $\frac{39}{2}$, $\frac{23}{2}$, $\frac{108}{2}$. It is easy to see that the equivalents, or rather atomic weights, of this system are identical with those in the last column of the preceding table.

According to the recent experiments of M. Regnault, the specific heat of crystallized silicium forms an exception to the law of Dulong and Petit: but this exception may be attributed to a peculiar molecular constitution resulting from the allotropic states of this element: for the former experiments of M. Regnault have taught us, that among the several allotropic modifications of carbon, there is but one, viz., lamp-black, whose specific heat satisfies the law in question,—whereas those of diamond and graphite, the allotropic states of which are similar to those of silicium, deviate from that law.†

In the next place, the new system of atomic weights is in harmony with the law of isomorphism, which requires that isomorphous bodies be represented by analogous formulæ. Thus cuprous sulphide, which is isomorphous with sulphide of silver, $\mathrm{Ag_2}\cancel{\mathrm{S}}$, is expressed in the new system by the formula $\cancel{\mathrm{Cu}}_2\cancel{\mathrm{S}}$, whereas Gerhardt assigned to it the formula $\mathrm{Cu_4}\cancel{\mathrm{S}}$. Again, the sulphates of silver and of sodium are represented by the analogous formulæ $\cancel{\mathrm{S}}\mathrm{Ag_2}\cancel{\mathrm{O}}_4$ and $\cancel{\mathrm{S}}\mathrm{Na_2}\cancel{\mathrm{O}}_4$. The isomorpbous sulphates of the magnesian series are expressed by the formula—

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* Berzelius wrote BaO, BaS, $BaO.H_2O$, $BaCl_2$, $BaSO_4$, &c. We return to these formulæ, but we agree with Gerhardt in writing K_2O, K_2S, KHO, KCl, K_2SO_4, &c.

† See on this point, the important remarks of Mr. Brodie on the atomic weight of graphite. Phil. Trans. 1859, p. 249.

$$\cancel{\mathrm{S}}\cancel{\mathrm{M}}\cancel{\mathrm{O}}_4 + 7\mathrm{H_2}\cancel{\mathrm{O}}.$$*

The composition of the double sulphates of the same series is respresented by the formula—

$$\cancel{\mathrm{S}}\cancel{\mathrm{M}}\cancel{\mathrm{O}}_4 \;.\; \cancel{\mathrm{S}}\mathrm{R_2}\cancel{\mathrm{O}}_4 + 6\mathrm{H_2}\cancel{\mathrm{O}}.$$

Lastly, the system of atomic weights which we adopt is in harmony with the vapour-densities of a very considerable number of bodies. The exceptions observed, relate to the vapour-densities of certain elementary bodies.† Thus the atomic weights of phos-

---

* A large number of salts contain quantities of water, which, in Gerhardt's notation, must be represented by a fractional number of molecules ($\mathrm{H_2}\cancel{\mathrm{O}} = 18$). Now this inconvenience is obviated if we double the atomic weights of a certain number of the metals, as may be seen by the following examples.—

Gerhardt's Notation.	New Notation.
$\mathrm{NiCl} + 4\tfrac12\ \mathrm{H_2}\cancel{\mathrm{O}}$	$\cancel{\mathrm{Ni}}''\mathrm{Cl_2} + 9\ \mathrm{H_2}\cancel{\mathrm{O}}$
$\left.\begin{matrix}\mathrm{Cu}\\ \mathrm{N}\cancel{\mathrm{O}}_2\end{matrix}\right\}\cancel{\mathrm{O}} + 1\tfrac12\ \mathrm{H_2}\cancel{\mathrm{O}}$	$\left.\begin{matrix}\cancel{\mathrm{Cu}}''\\ 2\mathrm{N}\cancel{\mathrm{O}}_2\end{matrix}\right\}\cancel{\mathrm{O}}_2 + 3\ \mathrm{H_2}\cancel{\mathrm{O}}$
$\left.\begin{matrix}\mathrm{Cu}\\ \cancel{\mathrm{C}}_2\mathrm{H_3}\cancel{\mathrm{O}}\end{matrix}\right\}\cancel{\mathrm{O}} + \tfrac12\ \mathrm{H_2}\cancel{\mathrm{O}}$	$\left.\begin{matrix}\cancel{\mathrm{Cu}}''\\ 2(\cancel{\mathrm{C}}_2\mathrm{H_3}\cancel{\mathrm{O}})\end{matrix}\right\}\cancel{\mathrm{O}}_2 + \mathrm{H_2}\cancel{\mathrm{O}}$
$\left.\begin{matrix}\mathrm{Pb}\\ \cancel{\mathrm{C}}_2\mathrm{H_3}\cancel{\mathrm{O}}\end{matrix}\right\}\cancel{\mathrm{O}} + 1\tfrac12\ \mathrm{H_2}\cancel{\mathrm{O}}$	$\left.\begin{matrix}\cancel{\mathrm{Pb}}''\\ 2(\cancel{\mathrm{C}}_2\mathrm{H_3}\cancel{\mathrm{O}})\end{matrix}\right\}\cancel{\mathrm{O}}_2 + 3\ \mathrm{H_2}\cancel{\mathrm{O}}$
$\left.\begin{matrix}\mathrm{Pb}\\ \mathrm{Cl}\cancel{\mathrm{O}}_3\end{matrix}\right\}\cancel{\mathrm{O}} + 1\tfrac12\ \mathrm{H_2}\cancel{\mathrm{O}}$	$\left.\begin{matrix}\cancel{\mathrm{Pb}}''\\ 2(\mathrm{Cl}\cancel{\mathrm{O}}_3\end{matrix}\right\}\cancel{\mathrm{O}}_2 + 3\ \mathrm{H_2}\cancel{\mathrm{O}}$
(Roscoe)	(Roscoe)

† The atomic weights of the elementary bodies (referred to 1 volume) are obtained by multiplying their vapour-densities by 14·44 $= \frac{1}{00693}$; and the molecular weights (referred to 2 volumes) are obtained by multiplying the vapour-densities by 28·88 $= \frac{2}{00693}$. But on multiplying the vapour-densities of mercury, 6·976, and of cadmium, 3·94, by 28·88, we find the numbers 201·4 and 113·7; and the anomaly exhibited by these metals may be expressed by saying, that their molecular weights, such as are deduced from their vapour-densities, really represent their atomic weights ($200 = \cancel{\mathrm{Hg}}$; $111{\cdot}5 = \cancel{\mathrm{Cd}}$). On the other hand, if we multiply the vapour-densities of phosphorus, 4·42, and of arsenic, 10·6, by 14·44, we obtain the numbers 63·8 and 153, an anomaly which may be expressed by saying, that the atomic weights of these bodies, as deduced from their vapour-densities, really express their molecular weights (PP = 63; As As = 150).

phorus, arsenic, mercury, zinc and cadmium, calculated from their vapour-densities, do not agree with those which are deduced from other considerations. These cases may, however, be regarded as exceptional, if we remember that the atomic weights of a large number of compounds into which these elements enter, are in accordance with the atomic weights in question. We will cite a few examples, confining ourselves to the diatomic and tetratomic metals :—

	Vapour-densities.	Molecular weights deduced from vapour-densities.	Molecular weights.	Formulæ.
Chloride of silicium .	5·939	171	170	$SiCl_4$
Chloride of zirconium	8·21	237		Zr_2Cl_4
Chloride of titanium .	6·836	197	190·2	$TiCl_4$
Stannic chloride . . .	9·2	265	260	$SnCl_4$
Stannethyl	8·021	232	234	$Sn(C_2H_5)_4$
Zinc-ethyl	4·259	123	124	$Zn(C_2H_5)_2$
Mercuric chloride . .	9·42	271	271	$HgCl_2$
Mercuric bromide . .	12·16	351	360	$HgBr_2$

If then we adopt for the metals in question, atomic weights twice as great as those usually assigned to them, and accordingly regard the metals as diatomic, we shall be able to compare oxide of ethylene with the oxides of these metals. This organic oxide thus becomes the analogue of baryta, just as oxide of ethyl is the analogue of oxide of silver, and oxide of glyceryl the analogue of oxide of antimony.

$$\left.\begin{matrix}Ag'\\ Ag'\end{matrix}\right\}O \qquad Ba''O \qquad \left.\begin{matrix}Sb'''\\ Sb'''\end{matrix}\right\}O_3$$

$$\left.\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right\}O \qquad C_2H_4O \qquad \left.\begin{matrix}C_3H_5\\ C_3H_5\end{matrix}\right\}O_3.$$

I. We know that caustic baryta is capable of absorbing oxygen and passing to a higher degree of oxidation, viz., the bioxide of barium. Oxide of ethylene possesses the same property, although the reaction takes place under different conditions, and the product, instead of being neutral, like bioxide of barium, exhibits the properties of an acid. When an aqueous solution of oxide of ethylene is placed in contact with platinum-black, the liquid rapidly becomes acid, in consequence of the formation of glycolic acid, which constitutes the product of the direct oxidation of oxide of ethylene. The glyoxylic acid of Dr. Debus may be regarded as a higher oxide of the same products, so that we may construct the following series:—

$\cancel{C}_2H_4$	ethylene.
$\cancel{C}_2H_4\Theta$	oxide of ethylene.
$\cancel{C}_2H_4\Theta_2$............	glycolic acid.
$\cancel{C}_2H_4\Theta_3$............	glyoxylic acid.

We are acquainted with other series of the same kind in organic chemistry, and these series, be it observed, have their analogues in mineral chemistry.

Laurent established the following series:*—

ClH	PH_3
$ClH\Theta$	$PH_3\Theta_2$
$ClH\Theta_2$	$PH_3\Theta_3$
$ClH\Theta_3$	$PH_3\Theta_4$
$ClH\Theta_4$	

and Odling developing this idea, has given other series of the same kind in his excellent "Manual of Chemistry."

II. Caustic baryta, to which we have just compared oxide of ethylene, unites directly with water to form hydrate of baryta. In like manner, oxide of ethylene is capable of fixing water, so as to form hydrate of oxide of ethylene, that is to say, glycol. Between the hydrates of organic chemistry and the hydrated oxides of mineral chemistry, we may establish the following parallel:—

$\left.\begin{matrix}K\\H\end{matrix}\right\}\Theta$	$\left.\begin{matrix}\cancel{B}a''\\H_2\end{matrix}\right\}\Theta_2$	$\left.\begin{matrix}Sb'''\\H_3\end{matrix}\right\}\Theta_3$	$\left.\begin{matrix}\cancel{Fe}^{vi}\ddagger\\H_6\end{matrix}\right\}\Theta_6$
Potassa.	Baryta.	Antimonic hydrate.	Ferric hydrate.
$\left.\begin{matrix}\cancel{C}_2H_5\\H\end{matrix}\right\}\Theta$	$\left.\begin{matrix}(\cancel{C}_2H_4)''\\H_2\end{matrix}\right\}\Theta_2$	$\left.\begin{matrix}(\cancel{C}_3H_5)'''\\H_3\end{matrix}\right\}\Theta_3$	$\left.\begin{matrix}(\cancel{C}_6H_8)^{vi}\\H_6\end{matrix}\right\}\Theta_6$
Alcohol.	Hydrate of ethylene. (glycol.)	Glycerin.	Hexylic hydrate (Mannite.)†

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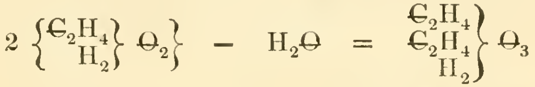
* Laurent's *Methode de Chemie,* translated by Odling, pp. 30, 31.

† Wanklyn and Erlenmeyer, Proceedings of the Royal Society, xi., 447.

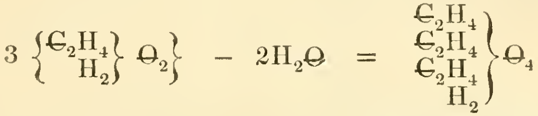
‡ $\cancel{Fe} = Fe^4 = 112$.

But oxide of ethylene exhibits this remarkable peculiarity, that not only is *one* molecule of it capable of uniting with one molecule of water, but *two, three, four, five*, or more, molecules of oxide of ethylene can combine with a single molecule of water, to form hydrates belonging to more and more complex types. These hydrates constitute the polyethylenic alcohols, the first of which, viz., diethylenic alcohol, was discovered by M. Lourenço. They may be regarded as resulting from the partial dehydration of an increasing number of molecules of glycol.



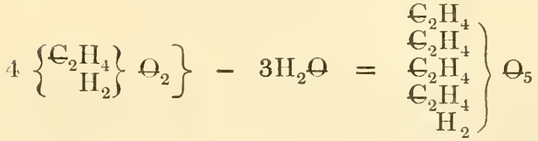
$$2\left\{\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2\right\} - H_2O = \left.\begin{matrix}C_2H_4\\C_2H_4\\H_2\end{matrix}\right\}O_3$$

Glycol. Diethylenic alcohol.



$$3\left\{\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2\right\} - 2H_2O = \left.\begin{matrix}C_2H_4\\C_2H_4\\C_2H_4\\H_2\end{matrix}\right\}O_4$$

Triethylenic alcohol.



$$4\left\{\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2\right\} - 3H_2O = \left.\begin{matrix}C_2H_4\\C_2H_4\\C_2H_4\\C_2H_4\\H_2\end{matrix}\right\}O_5$$

Tetrethylenic alcohol.

The study of these bodies establishes a new property of ethylene, the power of accumulating in combination, and thereby forming compounds containing multiple radicles, and belonging to types of greater and greater complexity. This property is likewise possessed by other organic radicles. M. Friedel and myself have found it in acetyl, which accumulates in the polyacetic compounds, and M. Lourenço has observed it in glyceryl, which in like manner is capable of forming polyglyceric compounds. It is, therefore, a general property of polyatomic radicles, and ought to be found, not only in certain mineral groups, but likewise in the elements of mineral chemistry which are the representatives of these radicles.

Amongst mineral groups possessing the property in question, we may mention *sulphuryl, chromyl,* and *phosphoryl,* which may be supposed to exist in the following compounds :—

$\left.\begin{matrix}\mathrm{S}\Theta_2\\ \mathrm{S}\Theta_2\\ \mathrm{H}_2\end{matrix}\right\}\Theta_3$	$\left.\begin{matrix}\mathrm{CrO}_2\\ \mathrm{CrO}_2\\ \mathrm{K}_2\end{matrix}\right\}\Theta_3$	$\left.\begin{matrix}(\mathrm{P}\Theta)'''\\ (\mathrm{P}\Theta)'''\\ \mathrm{H}_4\end{matrix}\right\}\Theta_5$
Nordhausen sulphuric acid.	Chromate of potassium.	Pyrophosphoric acid.

Amongst elementary bodies which play the part of polyatomic radicles, we shall here consider only *tin* and *silicium* both tetratomic and capable of forming polystannic and polysilicic compounds.

1. *Stannic hydrate*, to which Mr. Graham has just called attention in his remarkable researches on dialysis, contains

$$\left.\begin{matrix}\mathrm{Sn}^{\mathrm{iv}}\\ \mathrm{H}_4\end{matrix}\right\}\Theta_4,$$

and yields, with loss of $\mathrm{H}_2\Theta$, a hydrate containing

$$\left.\begin{matrix}\mathrm{Sn}^{\mathrm{iv}}\\ \mathrm{H}_2\end{matrix}\right\}\Theta_3,$$

which is the stannic acid dried in vacuo, analysed by M. Fremy.

The composition of the *stannates* is represented by the formula

$$\left.\begin{matrix}\mathrm{Sn}^{\mathrm{iv}}\\ 2\mathrm{R}'\end{matrix}\right\}\Theta_3.$$

Metastannic hydrate, according to M. Fremy, contains within its molecule 5 atoms of tin, so that its composition is expressed by the formula

$$\left.\begin{matrix}5\mathrm{Sn}^{\mathrm{iv}}\\ \mathrm{H}_{20}\end{matrix}\right\}\Theta_{20}.$$

At 100°, it gives off half its water, and is converted into a hydrate,

$$\left.\begin{matrix}5\mathrm{Sn}^{\mathrm{iv}}\\ \mathrm{H}_{10}\end{matrix}\right\}\Theta_{15}.$$

The *metastannates* are represented by the formula

$$\left.\begin{matrix}5\mathrm{Sn}^{\mathrm{iv}}\\ \mathrm{H}_8\mathrm{R}_2\end{matrix}\right\}\Theta_{15}.$$

We see then, that in metastannic hydrate and the metastannates, a number of atoms of tin are accumulated in one and the same molecule. The same property is exhibited by *silicium*, in various silicic hydrates and ethers, and in a very large number of silicates. This will be seen by a glance at the following table, in which the formulæ ranged on the same horizontal line afford examples of continually increasing condensation, whilst those in the same vertical column represent the hydrates, or rather anhydrides, formed successively by the loss of a continually increasing number of molecules of water:—

$\left.\begin{matrix}\mathrm{Si}^{iv}\\ \mathrm{H}_4\end{matrix}\right\}\mathrm{O}_4$	$\left.\begin{matrix}\mathrm{Si}\\ \mathrm{Si}\\ \mathrm{H}_8\end{matrix}\right\}\mathrm{O}_8$	$\left.\begin{matrix}\mathrm{Si}\\ \mathrm{Si}\\ \mathrm{Si}\\ \mathrm{H}_{12}\end{matrix}\right\}\mathrm{O}_{12}$	$\left.\begin{matrix}\mathrm{Si}_4\\ \mathrm{H}_{16}\end{matrix}\right\}\mathrm{O}_{16}$	„	$\left.\begin{matrix}\mathrm{Si}_6\\ \mathrm{H}_{24}\end{matrix}\right\}\mathrm{O}_{24}$
$\left.\begin{matrix}\mathrm{Si}\\ \mathrm{H}_2\end{matrix}\right\}\mathrm{O}_3$	$\left.\begin{matrix}\mathrm{Si}_2\\ \mathrm{H}_6\end{matrix}\right\}\mathrm{O}_7$	$\left.\begin{matrix}\mathrm{Si}_3\\ \mathrm{H}_{10}\end{matrix}\right\}\mathrm{O}_{11}$	$\left.\begin{matrix}\mathrm{Si}_4\\ \mathrm{H}_{14}\end{matrix}\right\}\mathrm{O}_{15}$	„	„
	$\left.\begin{matrix}\mathrm{Si}_2\\ \mathrm{H}_4\end{matrix}\right\}\mathrm{O}_6$	$\left.\begin{matrix}\mathrm{Si}_3\\ \mathrm{H}_8\end{matrix}\right\}\mathrm{O}_{10}$	$\left.\begin{matrix}\mathrm{Si}_4\\ \mathrm{H}_{12}\end{matrix}\right\}\mathrm{O}_{14}$	„	„
	$\left.\begin{matrix}\mathrm{Si}_2\\ \mathrm{H}_2\end{matrix}\right\}\mathrm{O}_5$	$\left.\begin{matrix}\mathrm{Si}_3\\ \mathrm{H}_6\end{matrix}\right\}\mathrm{O}_9$	$\left.\begin{matrix}\mathrm{Si}_4\\ \mathrm{H}_{10}\end{matrix}\right\}\mathrm{O}_{13}$	„	„
		$\left.\begin{matrix}\mathrm{Si}_3\\ \mathrm{H}_4\end{matrix}\right\}\mathrm{O}_8$	$\left.\begin{matrix}\mathrm{Si}_4\\ \mathrm{H}_8\end{matrix}\right\}\mathrm{O}_{12}$	„	„
		$\left.\begin{matrix}\mathrm{Si}_3\\ \mathrm{H}_2\end{matrix}\right\}\mathrm{O}_7$	$\left.\begin{matrix}\mathrm{Si}_4\\ \mathrm{H}_6\end{matrix}\right\}\mathrm{O}_{11}$	„	$\left.\begin{matrix}\mathrm{Si}_6\\ \mathrm{H}_8\end{matrix}\right\}\mathrm{O}_{16}$

$\left.\begin{matrix}\mathrm{Si}\\ (\mathrm{C}_2\mathrm{H}_5)_4\end{matrix}\right\}\mathrm{O}_4$ Normal silicic ether.	$\left.\begin{matrix}\mathrm{Si}_2\\ \mathrm{Ca}''\\ \mathrm{H}_4\end{matrix}\right\}\mathrm{O}_7$ Okenite.	$\left.\begin{matrix}\mathrm{Si}_3\\ \mathrm{Al}^{vi}\\ 2\mathrm{M}'\end{matrix}\right\}\mathrm{O}_{10}$* Ryacolite.	$\left.\begin{matrix}\mathrm{Si}_4\\ \mathrm{Al}^{vi}\\ 2\mathrm{M}'\end{matrix}\right\}\mathrm{O}_{12}$ Leucite.	„	$\left.\begin{matrix}\mathrm{Si}_6\\ \mathrm{Al}^{vi}\\ \mathrm{K}_2\end{matrix}\right\}\mathrm{O}_{16}$ Felspar (orthoclase.)
$\left.\begin{matrix}\mathrm{Si}\\ 2\mathrm{Mg}''\end{matrix}\right\}\mathrm{O}_4$ Olivine.	$\left.\begin{matrix}\mathrm{Si}\\ \mathrm{Ca}''\\ \mathrm{Mg}''\end{matrix}\right\}\mathrm{O}_6$ Diopside.				
$\left.\begin{matrix}\mathrm{Si}\\ \mathrm{C}(_2\mathrm{H}_5)_2\end{matrix}\right\}\mathrm{O}_3$ Diethylic silicate.	$\left.\begin{matrix}\mathrm{Si}_2\\ (\mathrm{C}_2\mathrm{H}_5)_2\end{matrix}\right\}\mathrm{O}_5$ Diethlyic disilicate.				

We see then that this theory enables us to conceive, and even to predict, the existence of a very large number of silicates, and that it is not without reason that these compounds have received the epithet *polysilicic.* Their constitution, and the formulæ which represent them, are not always very simple, and cannot be so in a great number of cases; but that which is really simple and rational is their mode of generation, based on the principle of the *accumulation of polyatomic radicles.* This principle, which likewise regulates the congregation of organic molecules, appears to be capable of a great number of applications in mineral chemistry, and is on this account well worthy of attention. We may also notice the part played, in the formation of these compounds, by the successive dehydration, of which hydrates containing polyatomic radicles are susceptible.

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* ~~Al~~ $= \mathrm{Al}^4 = 54{\cdot}8$

III. Oxide of ethylene unites directly with acids, forming salts which constitute the ethylenic ethers, or ethers of glycol. These reactions sometimes take place with great energy. Thus when oxide of ethylene is placed in contact with sulphuric acid, combination takes place, attended with a hissing noise and great evolution of heat. By operating with caution, and using an acid diluted with water, a nearly neutral liquid may be obtained, which remains in the syrupy state when evaporated. The combination of oxide of ethylene with acetic acid, also takes place at ordinary temperatures, producing monacetic or diacetic glycol, according as one or two molecules of acid enter into the reaction :—

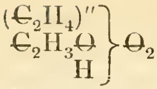
$$C_2H_4O \quad + \quad \left.\begin{matrix}C_2H_3O\\ H\end{matrix}\right\}O \quad = \quad \left.\begin{matrix}C_2H_4\\ (C_2H_3O)\\ H\end{matrix}\right\}O_2$$

$$C_2H_4O \quad + \quad 2\left\{\begin{matrix}C_2H_3O\\ H\end{matrix}\right\}O \quad = \quad \left.\begin{matrix}C_2H_4\\ (C_2H_3O)_2\end{matrix}\right\}O_2 + H_2O$$

Diacetic glycol may be formed directly by heating acetic anhydride with oxide of ethylene :—

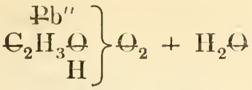
$$C_2H_4O \quad + \quad \left.\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}O \quad = \quad \left.\begin{matrix}C_2H_4\\ (C_2H_3O)_2\end{matrix}\right\}O_2.$$

Under these circumstances, then, oxide of ethylene behaves like a metallic oxide, and may be compared in this respect with oxide of copper or oxide of lead. When a single molecule of acetic acid acts upon oxide of lead, the so-called *bibasic acetate of lead* is formed, which may be compared with monoacetate of ethylene :—



$$\left.\begin{matrix}(Ꞓ_2H_4)'' \\ Ꞓ_2H_3Θ \\ H\end{matrix}\right\}Θ_2$$

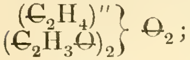
Monoacetate of ethylene.



$$\left.\begin{matrix}Pb'' \\ Ꞓ_2H_3Θ \\ H\end{matrix}\right\}Θ_2 + H_2Θ$$

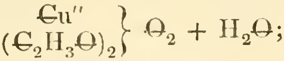
(so-called) Bibasic acetate of lead.

But when two molecules of acetic acid act upon a molecule of oxide of copper or oxide of lead, *neutral acetates* are formed comparable with ethylenic diacetate:—



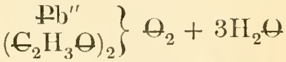
$$\left.\begin{matrix}(Ꞓ_2H_4)'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_2;$$

Ethylene diacetate.



$$\left.\begin{matrix}Ꞓu'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_2 + H_2Θ;$$

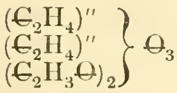
Diacetate of copper (Cristaux de Venus).



$$\left.\begin{matrix}Pb'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_2 + 3H_2Θ$$

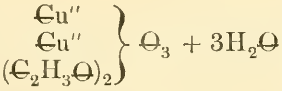
Diacetate of lead (Sal Saturni; sugar of lead)

But the analogy of all these reactions may be drawn still closer; for, just as several molecules of oxide of copper or oxide of lead can unite with acetic acid, so likewise may two, three, four, or more molecules of oxide of ethylene combine with acetic acid to form polyethylenic acetates. A glance at the following formulæ will be sufficient to show the analogy between the basic salts formed by certain mineral oxides, and these polyethylenic acetates:—



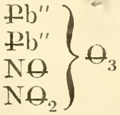
$$\left.\begin{matrix}(Ꞓ_2H_4)'' \\ (Ꞓ_2H_4)'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_3$$

Diethylenic acetate.



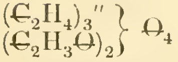
$$\left.\begin{matrix}Ꞓu'' \\ Ꞓu'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_3 + 3H_2Θ$$

Dicupricacetate.



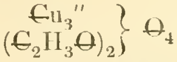
$$\left.\begin{matrix}Pb'' \\ Pb'' \\ NΘ \\ NΘ_2\end{matrix}\right\}Θ_3$$

Nitroso-nitrate of lead (Peligot's bibasic hyponitrate of lead).



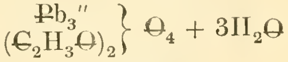
$$\left.\begin{matrix}(Ꞓ_2H_4)_3'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_4$$

Triethylenic acetate.



$$\left.\begin{matrix}Ꞓu_3'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_4$$

Tricupric acetate (heated to 160°).



$$\left.\begin{matrix}Pb_3'' \\ (Ꞓ_2H_3Θ)_2\end{matrix}\right\}Θ_4 + 3H_2Θ$$

Triplumbic acetate.

These basic salts owe their existence and formation to the tendency possessed by polyatomic radicles, both simple and compound, of accumulating in combinations. We are not acquainted with any well-defined basic salts formed by the union of monobasic acids with the oxides of potassium, sodium, lithium, and silver; and the power of forming basic salts, possessed by most other oxides, may, perhaps, be altogether dependent on the polyatomic nature of their metallic radicles. The following facts, however, exhibit this polyatomicity in a still clearer light:—

Oxide of ethylene possesses the power of uniting with two different monobasic acids. We are, in fact, acquainted with ethylenic ethers containing two different acid-radicles, such compounds having been obtained by Dr. Maxwell Simpson and M. Lourenço. In like manner there exist metallic salts produced by the reaction of two different monobasic acids on a diatomic oxide or hydrate. From this point of view, we may compare aceto-butyric glycol with nitro-acetate of strontium or baryta:—

$$\left.\begin{matrix}(Ꞓ_2H_4)''\\H_2\end{matrix}\right\}Ɵ_2 \qquad \left.\begin{matrix}Ꞩr''\\H_2\end{matrix}\right\}Ɵ_2 \qquad \left.\begin{matrix}Ƀa''\\H_2\end{matrix}\right\}Ɵ_2{*}$$

$$\left.\begin{matrix}(Ꞓ_2H_4)''\\Ꞓ_2H_3Ɵ\\Ꞓ_4H_7Ɵ\end{matrix}\right\}Ɵ_2 \qquad \left.\begin{matrix}Ꞩr''\\Ꞓ_2H_3Ɵ\\NƟ_2\end{matrix}\right\}Ɵ_2 \qquad \left.\begin{matrix}Ƀa''\\Ꞓ_2H_3Ɵ\\NƟ_2\end{matrix}\right\}Ɵ_2$$

In these compounds, the diatomic radicles, ethylene and strontium, perform exactly the same function as the diatomic radicle of tartaric acid in Rochelle salt, and the existence of the aceto-nitrate of strontium affords as strong an argument in favour of the double atomic weight of strontium, as that which was deduced by Liebig, from the existence of Rochelle salt, for doubling the formula of tartaric acid.

IV. Oxide of ethylene unites directly with chlorhydric acid. On mixing the two gases in equal volumes over mercury, they instantly disappear, just as ammonia gas disappears on being mixed with chlorhydric acid. The result of the combination is chlorhydrate of oxide of ethylene or chlorhydric glycol:—

$$\left.\begin{matrix}Ꞓ_2H_4\\H_2\end{matrix}\right\}Ɵ_2$$

Glycol.

$$\left.\begin{matrix}Ꞓ_2H_4\\H\end{matrix}\right\}\begin{matrix}Ɵ\\Cl\end{matrix} \qquad \text{or} \qquad Ꞓ_2H_4Ɵ.HCl$$

Mono-chlorhydric glycol.

Chlorhydrate of oxide of ethylene.

Is there in mineral chemistry any compound analogous to monochlorhydric glycol? I am not acquainted with any well defined metallic monochlorhydrin, but a sulphuric monochlorhydrin was discovered a few years ago by Professor Williamson:—

$$\left.\begin{matrix}SƟ_2\\H_2\end{matrix}\right\}Ɵ_2$$

Sulphuric acid.

$$\left.\begin{matrix}SƟ_2\\H\end{matrix}\right\}\begin{matrix}Ɵ_2\\Cl\end{matrix}$$

Sulphuric monochlorhydrin.

---

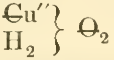
* C. v. Hauer, J. pr. Chem. lxxiv, 431.

On the other hand, several well defined fluorhydrins are known, viz., oxyfluorides, or fluorides of oxides. Thus Berzelius analysed a well crystallised oxyfluoride of copper, and expressed its composition by the formula, CuFl.CuO.HO, which if we adopt the double atomic weights of oxygen and copper, becomes

$$\text{Ꞓ}u''\text{Ɵ}\ .\ HFl$$

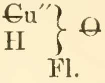
Fluorhydrate of cupric oxide.

It is easy to see that this compound is related to cupric hydrate in the same manner as monochlorhydric glycol to glycol:—



$$\left.\begin{matrix}\text{Ꞓ}u''\\ H_2\end{matrix}\right\}\text{Ɵ}_2$$

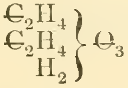
Cupric hydrate.



$$\begin{matrix}\left.\begin{matrix}\text{Ꞓ}u''\\ H\end{matrix}\right\}\text{Ɵ}\\ Fl.\end{matrix}$$

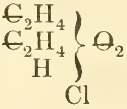
Cupric monofluorhydrin.

There exist condensed chlorhydrins corresponding to the polyethylenic alcohols. Diethylenic alcohol is capable of forming two chlorhydrins, whose composition is represented by the following formulæ:—



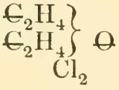
$$\left.\begin{matrix}\text{Ꞓ}_2H_4\\ \text{Ꞓ}_2H_4\\ H_2\end{matrix}\right\}\text{Ɵ}_3$$

Diethylenic alcohol.



$$\begin{matrix}\left.\begin{matrix}\text{Ꞓ}_2H_4\\ \text{Ꞓ}_2H_4\\ H\end{matrix}\right\}\text{Ɵ}_2\\ Cl\end{matrix}$$

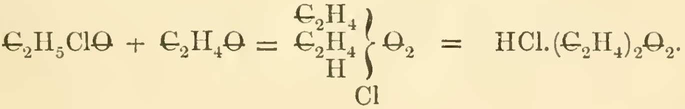
Monochlorhydrin of diethylenic alcohol.



$$\begin{matrix}\left.\begin{matrix}\text{Ꞓ}_2H_4\\ \text{Ꞓ}_2H_4\end{matrix}\right\}\text{Ɵ}\\ Cl_2\end{matrix}$$

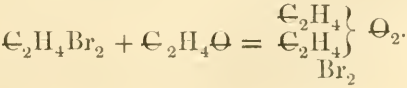
Dichlorhydrin of diethylenic alcohol.

The monochlorhydrin of diethylenic alcohol is obtained by heating chlorhydric glycol with oxide of ethylene:—



$$\text{Ꞓ}_2H_5Cl\text{Ɵ} + \text{Ꞓ}_2H_4\text{Ɵ} = \begin{matrix}\left.\begin{matrix}\text{Ꞓ}_2H_4\\ \text{Ꞓ}_2H_4\\ H\end{matrix}\right\}\text{Ɵ}_2\\ Cl\end{matrix} = HCl.(\text{Ꞓ}_2H_4)_2\text{Ɵ}_2.$$

It is a liquid boiling at about 180°. The dibromhydrin of diethylenic alcohol is probably formed when oxide of ethylene is boiled for a long time with bromide of ethylene (unpublished experiments):—



$$\text{Ꞓ}_2H_4Br_2 + \text{Ꞓ}_2H_4\text{Ɵ} = \begin{matrix}\left.\begin{matrix}\text{Ꞓ}_2H_4\\ \text{Ꞓ}_2H_4\end{matrix}\right\}\text{Ɵ}_2.\\ Br_2\end{matrix}$$

This last compound may be compared with the bromides and chlorides of mineral oxides. It will be interesting to establish this analogy by a few examples.

Hydrate of lime dissolves in a solution of chloride of calcium, and the alkaline liquid, when concentrated, yields on cooling hydrated crystals, to which H. Rose assigns the formula $\mathrm{3CaO.CaCl} + \mathrm{16HO}$. In our notation, this formula becomes $\mathrm{3CaO.CaCl_2} + \mathrm{16H_2O}$, and may be written as follows:—

$$\begin{matrix}\left.\begin{matrix}\mathrm{Ca}\\ \mathrm{Ca}\\ \mathrm{Ca}\\ \mathrm{Ca}\end{matrix}\right\}\mathrm{O_3}\\ \mathrm{Cl_2}\end{matrix} + \mathrm{16H_2O}, \text{ which is analogous to } \begin{matrix}\left.\begin{matrix}\mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{C_2H_4}\end{matrix}\right\}\mathrm{O_3}\\ \mathrm{Cl_2}\end{matrix}$$

Dichlorhydrin of tetrethylenic alcohol.

There are also oxychlorides of lead possessing an analogous constitution. Thus *Mendipite*, which is a well crystallised mineral, contains

= PbO + PbCl

$$\mathrm{2PbO.PbCl_2} = \begin{matrix}\mathrm{Pb_3O_2}\\ \mathrm{Cl_2}.\end{matrix}$$

Atacamite is a hydrated oxychloride of copper composed of

3 CuO . CuCl

$$\mathrm{3CuO.CuCl_2} = \begin{matrix}\mathrm{Cu_4O_3}\\ \mathrm{Cl_2}.\end{matrix}$$

Other facts belonging to mineral chemistry may likewise be compared with the preceding. Thus the compounds formed when ferric oxide is dissolved in a solution of ferric chloride (and we know that it dissolves abundantly) are doubtless analogous to the chlorhydrins. On the other hand, H. Rose has shewn that the solution, obtained by treating stannic chloride with water, possesses characters totally different from those which are exhibited by the chlorhydric solution of metastannic acid.* From the molecular constitution of this acid, we may suppose that its chlorhydric solution contains a polystannic chlorhydrin.

V. Dr. Maxwell Simpson has described, under the name of glycolic chloraceten (aceto-chlorhydric glycol) a mixed ether of glycol, which he has obtained by subjecting that body to the simultaneous† action of acetic and chlorhydric acids. This compound contains $\left.\begin{matrix}(\cancel{C}_2H_4)'' \\ (\cancel{C}_2H_3\Theta)'\end{matrix}\right\}\begin{matrix}\Theta \\ \mathrm{Cl}\end{matrix}$; or, as it may be more simply written, $\left.\begin{matrix}(\cancel{C}_2H_4)'' \\ (\cancel{C}_2H_3\Theta)'\end{matrix}\right\}\begin{matrix}\Theta \\ \mathrm{Cl}.\end{matrix}$

---

* Pogg. Ann. cv. 564.

† Proceedings of the Royal Society, ix, 725.

We are acquainted with certain mineral compounds of analogous constitution, excepting that in place of acetyl, they contain polybasic acid radicles. Thus *Wagnerite* and *Apatite*, which are well characterised mineral species, are fluophosphates of magnesium and calcium, to which we may assign the formulæ

$$PO_5.3MgO + MgFl \text{ and } 3(PO_5.3CaO) + CaFl,$$

which in our notation become

$$\underset{\text{Wagnerite.}}{\left.\begin{matrix}(P\Theta)''' \\ 2\cancel{Mg}''\end{matrix}\right\}\begin{matrix}\Theta_3 \\ Fl\end{matrix}} \quad \text{and} \quad \underset{\text{Apatite.}}{\left.\begin{matrix}3(PO)''' \\ 5\cancel{Ca}''\end{matrix}\right\}\begin{matrix}\Theta_9 \\ Fl\end{matrix}}$$

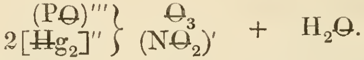
Wagnerite and Apatite are in fact the phosphofluorhydrins of the hydrates

$$\left.\begin{matrix}(P\Theta)''' \\ H_5\end{matrix}\right\}\Theta_4 \quad \text{and} \quad \left.\begin{matrix}(P\Theta)_3''' \\ H_{11}\end{matrix}\right\}\Theta_{10}.$$

And here we have occasion for an important remark. Ordinary phosphoric $\left.\begin{matrix}(P\Theta)''' \\ H_3\end{matrix}\right\}\Theta_3$ requires to saturate it more than one atom of magnesium ($\cancel{Mg}'' = 24$), but two atoms of this magnesium, which are equivalent to four atoms of hydrogen, are too much for the purpose. Now, Wagnerite contains exactly two atoms of magnesium; it would therefore be supersaturated if the fourth combining unit of the group $2\cancel{Mg}''$ were not saturated by the fluorine. The same reasoning applies to apatite and to the calcium contained in it. We see, therefore, that in these compounds, whose constitution appears so strange when regarded from the dualistic point of view, the fluorine or the chlorine plays an important and necessary part. I may add, that the presence of such a monatomic element in these compounds furnishes an argument in favour of the diatomicity of magnesium and of calcium. If magnesium were monatomic, the fluorine would be useless; for 3Mg [Mg = 12] could replace 3H in ordinary phosphoric acid. But the magnesium or the calcium being diatomic, and therefore of even atomicity, the presence of a monatomic element becomes necessary to fill up the uneven atomicity of the phosphoryl $(P\Theta)'''$.*

Other compounds may likewise be regarded from this point of view. There exists a chlorophosphate of lead exactly analogous in constitution to apatite, and we know that the phosphoric acid in this chlorophosphate may be replaced by arsenic acid.

Gerhardt has analysed a mercurous nitrophosphate which contains a molecule of mercurous phosphate united with a molecule of mercurous nitrate. This compound, represented by the formula $Hg_2O.NO_5 + 3Hg_2O.PO_5 + 2HO$ may be considered a kind of Wagnerite, in which the magnesium is replaced by mercurosum $[\text{Ħ}g_2 = 400]$, and the fluorine by nitrous vapour :—



$$\left.\begin{matrix}(P\Theta)''' \\ 2[\text{Ħ}g_2]''\end{matrix}\right\}\begin{matrix}\Theta_3 \\ (N\Theta_2)'\end{matrix} + H_2\Theta.$$

VI. Just as the diatomic radicle, ethylene can join together two molecules of water, when it takes the place of two atoms of hydrogen to form glycol, so likewise is it capable of uniting two molecules of ammonia to form ethylene-diamine. I do not intend to give in this place a general view of the ethylenic polyamines—for our knowledge of which we are indebted to the classic researches and rare sagacity of Dr. Hofmann—but merely to call attention to the analogy existing between these compounds and certain mineral polyamines.

Diatomic metals are capable of replacing ethylene in the diamines. Compounds of this kind are known, and rational formulæ, for expressing the constitution of various metallic polyamines, have lately been proposed by MM. Weltzien and Hugo Schiff. I shall consider in this place only the formulæ given by Schiff for the cupric amines, viz.:—

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* My friend Dr. Odling has called my attention to a salt described by Briegleb (Ann. Ch. Pharm. xcviii. 95), and represented by the formula $3NaO.PO_5 + NaFl + 24HO$. Without attempting to deny that the existence of this salt may weaken the argument afforded by the constitution of Wagnerite in favour of the diatomicity of magnesium, I will nevertheless observe: 1. That the salt is very unstable, being resolved, by boiling, into phosphate and fluoride. 2. That it has not been found possible to form a corresponding salt of potassium. 3. That this salt is not strictly comparable with Wagnerite, inasmuch as it contains water of crystallisation.

We are indebted to M. Cannizzaro for another chemical argument in favour of the diatomicity of calcium and barium—namely, that whereas there exists a quadroxalate of potassium, we are not acquainted with a quadroxalate of calcium or of barium. In fact, a single atom of hydrogen in two molecules of oxalic acid may be replaced by an atom of potassium, but not by an atom of diatomic calcium, which is equivalent to two atoms of hydrogen. If then a portion of the hydrogen in two molecules of oxalic acid is replaced by calcium or barium, the result of the substitution can only be a bioxalate.

$$\mathrm{N}\left\{\begin{matrix}\mathrm{Cu}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right. \qquad \text{and} \qquad \mathrm{N}\left\{\begin{matrix}\mathrm{Cu}\\ \mathrm{Am}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right.$$

Cupriconium. Amicupriconium.

I double these formulæ, and suppose that in the cupric diamines, the diatomic radicle, copper, joins together two molecules of ammonium, just as ethylene does in ethylenic diammonium. I therefore write the formulæ of the cupric diammoniums as follows:—

$$\mathrm{N}_2\left\{\begin{matrix}(\text{Ꞓ}_2\mathrm{H}_4)''\\ \mathrm{H}_2\\ \mathrm{H}_2\\ \mathrm{H}_2\end{matrix}\right.$$

Ethylene-diammonium.

$$\mathrm{N}_2\left\{\begin{matrix}\text{Ꞓ}\mathrm{u}''\\ \mathrm{H}_2\\ \mathrm{H}_2\\ \mathrm{H}_2\end{matrix}\right.$$

Cupriconium.

$$\mathrm{N}_2\left\{\begin{matrix}\text{Ꞓ}\mathrm{u}''\\ \mathrm{Am}_2\\ \mathrm{H}_2\\ \mathrm{H}_2\end{matrix}\right.$$

Diamicupriconium.

$$\mathrm{N}_2\left\{\begin{matrix}\text{Ꞓ}\mathrm{u}''\\ \mathrm{Am}_2\\ \mathrm{Am}_2\\ \mathrm{H}_2\end{matrix}\right.$$

Tetramicupriconium.

$$\left.\begin{matrix}\left[\mathrm{N}_2\left\{\begin{matrix}\text{Ꞓ}\mathrm{u}''\\ \mathrm{H}_6\end{matrix}\right.\right]''\\ (\text{Ꞓ}_2\mathrm{H}_3\Theta)_2\end{matrix}\right\}\Theta_2 + 2\mathrm{H}^2\Theta$$

Acetate of cupriconium.

$$\left.\begin{matrix}\left[\mathrm{N}_2\left\{\begin{matrix}\text{Ꞓ}\mathrm{u}''\\ \mathrm{Am}_4\\ \mathrm{H}_2\end{matrix}\right.\right]''\\ (\text{Ꞩ}\Theta_2)''\end{matrix}\right\}\Theta_2 + 2\mathrm{H}\Theta_2$$

Sulphate of Tetramicupriconium (ammonio-sulphate of copper).

Besides the ethylene-bases, we are acquainted with another class of bases, called *oxyethylenic.* They are formed by the direct combination of oxide of ethylene with ammonia. One, two, three, four molecules of oxide of ethylene can unite with a single molecule of ammonia to form bases of greater and greater complexity, and this combination takes place at ordinary temperatures, energetically and without elimination of water: so great is the combining power of oxide of ethylene. It appears to me—and with this consideration I will conclude—that there exist in mineral chemistry bases analogous to the oxyethylenic bases. M. Millon discovered, some years ago, a remarkable base, to which he gave the name of *ammonio-mercuric oxide.* It is formed by the action of ammonia on mercuric oxide. Its composition is usually represented by the formula $3\mathrm{HgO.HgH_2N} + 3\mathrm{HO}$, which, translated into our notation, independently of any hypothesis respecting the molecular arrangement, becomes—

$$2HgO.NH_3 + H_2O;$$

according to which, ammonio-mercuric oxide would be the analogue of *dioxethylenamine*—

$$2(C_2H_4O).NH_3.$$

According to the experiments of M. Millon, this base can give off more than one molecule of water in drying, and, when perfectly dry, contains $3HgO.HgN_2H_2$, or, in our notation, $3HgO.HgN_2H_4$. Here again we may perceive a certain analogy between these facts and those which are observed in organic chemistry; we know indeed that the oxyethylenic bases are converted, by loss of water, into vinylic bases.

Such are the considerations which I have ventured to put forward on the analogies existing between organic and mineral compounds. I have endeavoured to follow out these analogies in the most various classes of bodies, and to express them in the typical notation, so well adapted to comparisons of this nature. I shall think myself happy if I have succeeded in impressing more forcibly on the minds of my auditors this truth, which everybody is ready to enunciate, but which few have undertaken to establish by strict demonstration—namely, that *there is but one Chemistry, and that the laws which regulate the constitution of Organic bodies apply with equal force to the compounds of Mineral Chemistry and Mineralogy.*

XLIX.—*On the Chemistry of Digestion.*

[A Discourse delivered to the Fellows of the Chemical Society.]

By W. Marcet, M.D., F.R.S.,

Assistant Physician to the Westminster Hospital, etc.

By the chemical phenomena of digestion, we mean those chemical changes which food undergoes in the stomach and intestines, the object of which is to transform it into certain soluble substances on the one hand, and into emulsions on the other; for under those conditions only, can the food taken be absorbed into the blood-vessels and lacteals, and thereby effect the purpose of nutrition. If from some circumstance connected with the nature of the ingesta, or a vitiated state of the gastric and intestinal secretions, the metamorphosis in question does not take place, what has been eaten will be voided, more or less unaltered,—a fact of importance in a medical point of view.

My attention has been directed for many years to the subject of the present discourse, and I avail myself, with pleasure, of this opportunity of recording the valuable aid of my former assistant, Dr. Frederick Dupré, in a considerable portion of these inquiries.

The stomach, during the period of fasting, contains a small quantity of mucus, exhibiting a slight, though decided, alkaline reaction; this can be easily ascertained by testing the few drops of the ropy and frothy fluid obtained from the stomach of a dog having a gastric fistula, or external opening in that organ. As soon as solid food is taken, the stomach secretes in abundance a strongly acid fluid, the gastric juice, and the process of digestion commences. The action of the gastric juice on the contents of the stomach is generally considered as due to its acid constituent, and to a substance called *pepsin,* which it contains in very small quantity. It should be remembered, however, that every one of the constituents of gastric juice must have a share in its action on food; just in the same way as certain therapeutical agents, such as mineral waters, are possessed of medicinal properties, partly on account of a special substance they contain, and partly from the united influence of the whole of their constituents. Owing to this circumstance, it is important when experimenting on gastric juice, to use, as far as possible, the secretion obtained from an animal, such as the dog, and avoid conducting the inquiry with a digestive fluid prepared artificially by mixing together a dilute acid and pepsin. I invariably used in my researches the gastric juice of four dogs, extracted from each animal through a gastric fistula with which it had been provided. The secretion was excited with hard-boiled cartilage, or soft bones. By this means I obtained, from two dogs, about a gallon of gastric juice; and a much larger amount could have been extracted within the same time, had it been required.

In order to determine the composition of pure gastric juice, it would be necessary to excite its secretion by means of hard substances, perfectly insoluble in that fluid: unfortunately, under those circumstances, as for instance, when dogs are made to swallow pebbles, the quantity of gastric juice secreted is but very small, and barely sufficient for a chemical inquiry. It must be remembered that hard animal tissues, such as cartilage, or even bone, are rapidly acted upon by gastric juice, so much so, that the fluid obtained from the stomach after the ingestion of these substances cannot be regarded as the pure secretion.

The acidity of gastric juice may be considered as one of its characteristic features. It is remarkable that chemists and physiologists do not yet agree as to the nature of this free acid, although, from the investigations of Bidder and Schmidt, Dr. Prout's opinion on the subject now prevails, and the acid substance is believed to be hydrochloric acid; the experiment which Bidder and Schmidt undertook in order to resolve the question, was as follows:—

"About 100 grammes of gastric juice were used, to which nitric acid and nitrate of silver were added; the amount of chloride of silver obtained was determined, which yielded the weight of the whole of the hydrochloric acid present. After the excess of nitrate of silver had been removed from the gastric juice by precipitation with hydrochloric acid, the fluid was evaporated to dryness, carefully incinerated, and the weight of the bases determined; the quantity of hydrochloric acid necessary to neutralize these bases was then calculated." By so doing, Messrs. Bidder and Schmidt obtained, on the one hand, the weight of the whole of the hydrochloric present in gastric juice, and on the other, the weight of the hydrochloric acid necessary to neutralize the bases; and as they found that the total amount of hydrochloric acid present was greater than was necessary to neutralize the bases, they concluded that gastric juice contained some free hydrochloric acid. In order to decide whether there was any free acid in gastric juice besides hydrochloric acid, these enquirers determined the acidity of gastric juice with an alkaline normal solution, and they found the amount of the base necessary for the neutralization of this free acid to be exactly, or nearly equivalent to the quantity of free hydrochloric present, which had been ascertained in the first part of the experiment; they therefore concluded that the whole of the free acid of gastric juice is hydrochloric acid.

Notwithstanding the apparent correctness of this method of investigation, the gastric juice of a dog on which I have experimented, has appeared to me, for the following reason, to contain more or less of another acid besides hydrochloric acid. I happened to place some gastric juice in Graham's dialyser, which was made to float on distilled water. After a time, the secretion contained in the dialyser had lost certain of its immediate principles, which had passed into the distilled water. At first the acid gastric juice gave an abundant precipitate with nitrate of silver, but the bulk of the precipitate gradually diminished, the hydrochloric acid passing into the distilled water; and, finally, after coagulating the albumin by heat, and filtering, the addition of the reagent failed to give even a trace of a precipitate, thereby showing that the hydrochloric acid had entirely found its way through the membrane. On testing the fluid in the dialyser at that period of the experiment, it exhibited a distinctly acid reaction; consequently the gastric juice was still acid, although it did not contain a trace of hydrochloric acid, showing that another acid was present besides the hydrochloric acid.

The acidity of gastric juice, according to Bidder and Schmidt, ranges from 0·1708 to 0·3353 % of hydrochloric acid. I have had frequent opportunities of testing the degree of acidity of this secretion, and have found it to correspond to between 0·085 and 0·303 % of hydrochloric acid; these numbers, being rather lower than those of Bidder and Schmidt. While enquiring into the acidity of gastric juice, I observed that the degree of this re-action varied according to the period after the ingestion of food, at which the fluid was collected. The first quantity removed from the stomach was the most abundant, but the least acid; gradually less and less of the secretion could be obtained, but it became more and more acid; while the last quantities of the gastric juice which were extracted exhibited the maximum degree of acidity. The following is a table showing the quantities of gastric juice extracted from a dog bearing a gastric fistula, at different periods after the animal was fed, and also the degree of acidity of the fluid, expressed as potash, necessary to neutralize 100 CC. of the secretion. In four experiments the acidity invariably increased, so much so that the degree of acidity was considerably greater towards the close of each experiment than it was at the beginning.

Acidity of Gastric Juice.

The *time* is counted just after the dog took his meal, consisting of boiled wind-pipe. The *acidity* is expressed in grammes of potash necessary to neutralize 100 CC. of gastric juice. The experiments were made in middle of March, 1860.

Time after food taken.	Quantity.	Acidity.
	No. I.	
30 minutes	2oz.	0·065
40^{m} later	1oz.	0·113
	No. II.	
30 minutes	lost.	
30^{m} later	2oz. 2dr.	0·130
10^{m} later	7dr.	0·156
10^{m} later	6dr.	0·169
10^{m} later	5dr.	0·195
	No. III.	
30 minutes	7dr.	0·208
30^{m} later	1oz. 6dr.	0·227
30^{m} later	1oz.	0·273
30^{m} later	3dr.	0·377
30^{m} later	1oz. 5dr.	0·390
	No. IV.	
39 minutes	2oz. 6dr.	0·180
10^{m} later	1oz. 3dr.	0·190
17^{m} later	2oz. $\frac{1}{2}$dr.	0·235
15^{m} later	1oz. 4dr.	0·250
8^{m} later	5dr.	not determined.

This gradual increase of the acidity of gastric juice must be due, partly to the first quantities which are secreted being diluted and neutralized by the slightly alkaline mucus contained in the fasting stomach; but more especially, I believe, because the fluid secreted towards the end of digestion, is really more acid than that secreted at the beginning. This last hypothesis appears probable, if it be remembered that the mucus of the stomach, during the period of fasting, is but slightly alkaline, and exists therein but in small quantity. Whatever be the cause of the fact, the gradually increasing acidity of gastric juice, after food has been taken, appears established, and must serve some important purpose in connection with the process of digestion, one of these objects being obviously to add to the power of the stomach of digesting those pieces of food which have not been properly masticated. The outside of each morsel of animal food, which has been masticated, will not require for its digestion the action of strong gastric juice; but the inside of the morsel, especially in the case of animals, which is not so well triturated with the teeth, will require for its digestion the action of a more powerful or more acid gastric juice.

If we consider the average acidity of gastric juice to be due to the presence of 0·253 % of hydrochloric acid; and, if it be admitted, with Bidder and Schmidt, that an adult man, weighing about ten stone, secretes in twenty-four hours about 6400 grammes of gastric juice, then no less than about sixteen grammes (247 grns.) of free hydrochloric acid will be extracted from a human adult's blood, and returned into it in twenty-four hours. This acid must result from the decomposition of chloride of sodium, as was suggested by Prout* in 1834; but he adds "What becomes of the soda from which the muriatic acid has been disunited?" He proceeds to state, as his belief, that the largest part of this soda is probably directed to the liver, and passes off in the bile. We are now aware that such is not the case, and Dr. Bence Jones, by his researches on the acidity of the urine during the period of digestion and fasting, has solved this interesting question.† Blood is always alkaline; it must be so for the maintenance of health.‡ There is, however, in the blood a constant tendency to the formation of acid; but, before the blood can turn acid, the excess of this substance is eliminated by the secretions; consequently acids are constantly being secreted from the blood, sometimes in the perspiration, sometimes in the urine, sometimes by the stomach. When the secretion of acid in the urine is active, that of the stomach is quiescent, and *vice versâ;* during the secretion of gastric juice, the acidity of the urine is greatly diminished. At the time when digestion is at its height, the acidity of the urine is at its minimum. These are the interesting results of Dr. Bence Jones' inquiries. We may therefore surmise that, during digestion, the chloride of sodium of the blood yields hydrochloric acid to the gastric juice, while the soda is immediately taken up by the acid, which, during fasting would have been excreted with the urine, but which remains in the circulation while digestion is going on.

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* Chemistry, &c., of Digestion, 1834, p. 500.

† Phil. Trans. 1849.

‡ Dr. Pavy has observed that, after phosphoric acid has been injected into the circulation, the urinary secretion contains sugar.

If chloride of sodium be the source of the principal constituent of the gastric juice—*hydrochloric acid*—this salt must be one of the most important immediate principles of the blood; and we can understand, why, when animals are for a time comparatively deprived of chloride of sodium in their food, they eliminate none of this salt in their excrementitious secretions; and, consequently, in such cases, the same hydrochloric acid serves over and over again for the gastric secretion, while all the other constituents of the body are undergoing the normal process of waste. This is one of those admirable provisions of nature which have fitted animal life to be preserved under so many different circumstances.

The main object of the gastric digestion is the transformation of albuminous food into a substance which Lehmann has called *peptone,* and the conversion of neutral fats into fatty acids. Albumin, fibrin, casein, gelatin, and chondrin are modified in the stomach, and assume new characters, obviously in great measure with a view to their more ready absorption into the blood. Under the influence of the gastric juice, albuminous or protein-compounds lose their coagulability by heat and mineral acids, and likewise their property of forming insoluble combinations with most metallic salts. Lehmann has been unable to discover any difference between the quantities of nitrogen, carbon, oxygen, and sulphur contained in the peptone and in the substance from which it was derived. As to cartilage and gelatigenous bodies, they are converted in the stomach into substances which, according to Lehmann, correspond perfectly in their physical, and in most of their chemical properties to the peptones of the protein-bodies. We gather from the observations of this chemist, that, in his opinion, the various peptones derived from protein and gelatin compounds are sufficiently analogous to be considered as one and the same body. Peptones must be looked upon as modifications of albumin, fibrin, casein, gelatin, and chondrin, approximating to albumin of blood; indeed they are partly assimulated compounds.

Although I have no reason whatever to disbelieve Lehmann's views regarding the analogy existing between the chemical characters of peptones, still they do not appear to agree altogether in their physical properties; and this point is one of much interest. Some peptones, or perhaps only one kind of peptone, acts on polarised light, rotating the plane of polarisation to the left, while others appear to exhibit no such property.

I observed, in the spring of 1860, that gastric juice acts on polarised light; and for the following twelve months I diligently inquired into the various circumstances connected with this phenomenon. Shortly after my results had been communicated to this Society, I found in Henle and Meissner's "Bericht über die Vortschritte der Anatomie und Physiologie," for 1859, that Hoppe had already observed this same optical property of the gastric fluid; and I willingly give up to him the priority of the discovery; at the same time it should be understood that Hoppe merely detected the bare fact, and only expressed an opinion on its cause, based on one experiment. He believed this phenomenon to be due to a substance secreted in the gastric juice, while I have shown that it is owing to a product of the digestion of animal food, or a *peptone*.

There are two different animal tissues, which, when submitted to the action of gastric juice, in or out of the body, yield polarising peptone—these are cartilage and the mucous tissue of boïled intestines, which can be easily separated from the muscular tissue. I could obtain none, or no appreciable quantity of this substance, from pure coagulated albumin or coagulated casein, when digested in gastric juice out of the body. My experiments on the digestion of meat out of the body, have failed to give me any clear results, although dogs fed exclusively on cooked beef-steaks for a week, invariably yielded a gastric fluid which acted on polarised light. We can be sure that the constituent of gastric juice which thus rotates the plane of polarisation of light, is a *peptone* and not a *substance secreted;* for if, after keeping a dog fasting for thirty hours or longer, and then washing out his stomach thoroughly with water, the animal be made to swallow silicious pebbles, the small quantity of gastric juice secreted has no power of rotating the polarised ray. The result of this experiment is at variance with that obtained by Hoppe, who, after allowing an animal to fast, excited the gastric secretion with a glass rod, without however, taking the precaution of washing the stomach, and found that the fluid acted on polarised light. After exciting the secretion with fragments of bone, I obtained a gastric fluid which exerted but a very slight influence on polarised light, showing only seven divisions to the left in Soleil's saccharometer, while when the secretion was excited by cartilage, the rotation was from thirty to forty divisions, obviously from the digestion of the cartilage; and moreover, gastric juice, mixed with cartilage or with the internal tissue of boiled tripe, and exposed in a water-bath to a temperature equal to that of the body, acquires, after a short time, a power of deviating the plane of polarisation, which may be twice as great as that it possessed before the commencement of the artificial digestion.

After many experiments as to the best method of extracting from the gastric fluid the peptone under consideration, I succeeded in preparing it in a comparatively pure state, and then found it to be quite similar in its chemical properties to Lehmann's peptone. Four experiments were made with the dry substance in order to determine its rotatory power in Soleil's saccharometer. Solutions of the peptone in twenty-five cubic centimetres of water yielded for 1°, or division of the instrument, 0·020, 0·023, 0·027, 0·029 grammes: average 0·024 grm. Therefore, when gastric juice is examined in the saccharometer, for every degree of rotation to the left, the fluid contains 0·024 grm. of polarising peptone, or a proportion closely approximating to that, in twenty-five cubic centimetres.

Besides its office of transforming meat and allied articles of food into soluble substances, the stomach is possessed of another power no less important for the purposes of nutrition. I have discovered that it has the property of converting neutral fats, containing stearin, margarin, and butyrin, into their corresponding fatty acids; this fact, simple as it appears, is the key to the explanation of the digestion of fats. The fats of food are constantly neutral, they are not acidified by the process of cooking, although heated even for a length of time in contact with the acid juice of flesh, and as fatty acids are found in the stomach, it must be owing to a phenomenon of gastric digestion. If a dog bearing a gastric fistula be made to eat butter, the fluid extracted through the fistula a quarter of an hour or twenty minutes later, or even less, will smell strongly of butyric acid. The fat of beef or mutton, after having remained for a certain time in the stomach, yields to alcohol, although not to water, an acid reaction. When the food taken contains but little fat, the whole of it, perhaps, is acidified during the gastric digestion; in those cases where much fat is ingested, I believe a part of it escapes from the stomach, without having undergone any change. With respect to the olein of food, I had concluded in a paper I communicated to the Royal Society, in 1858, that this substance is not acidified in the stomach, but I do not wish to be too positive regarding this statement.

The importance of the transformation of neutral fats into fatty acids in the stomach will be readily understood, if we take into consideration the action of bile upon these substances, the characteristic physiological property of that secretion being its power of converting fatty acids into an emulsion, while, with regard to neutral fats, it exhibits no such influence: consequently fats undergo in the stomach a certain transformation, by which means the bile becomes capable of acting upon them, and transforming them into an emulsion.

I must now beg to make a few observations on the phenomenon of fatty emulsions.

When neutral fats or fatty acids in a fused condition are agitated with water, no emulsion is formed, but large globules are seen to pervade the fluid; on standing they immediately run into each other, and rise to the surface, the aqueous fluid remaining perfectly clear. When fused *neutral fats* are agitated with a solution of neutral tribasic phosphate of soda, I have observed the same phenomenon to take place as with pure water, but when fused *fatty acids* are treated with a solution of phosphate of soda, an emulsion is formed, or in other words, the globules of fat lose the property of running into each other; they remain separate, the fluid assuming a milky appearance: consequently phosphate of soda does not act equally on neutral and on fatty acids. This subject appearing to me of great interest, I have given it much attention, and I have found that the emulsion produced by acting on fatty acids with phosphate of soda is invariably accompanied by the formation of a certain quantity of soap; and a fact worthy of note is that the formation of soap persists, although, from the neutral phosphate becoming transformed into an acid phosphate, the emulsion is suspended in an acid fluid.

Emulsions of fat are also produced when bile and fused fatty acids are agitated together, or when pancreatic juice is shaken with both neutral or acid fats. This state of emulsion or of minute division of fats is indispensable for their absorption in the blood; an inquiry into the real nature of an emulsion would be therefore an object of much importance. Is it not something more than a mere mechanical division of fats into very small globules? I believe there are strong grounds for the assumption that there can be no emulsion without a chemical action, which may be conceived to take place in the following way:—When fused fatty acids are shaken in a test-tube with phosphate of soda or bile, the fat is instantly divided by a mechanical process into very minute globules, just as would happen if the fat was agitated with water; but at that moment each of these very small fatty particles becomes surrounded with a layer of soap, from the surface of the globule being saponified by the phosphate of soda or bile. From this circumstance the globules of fat lose their property of running into each other, and acquire a slight increase of specific gravity, which however is not sufficient to prevent them from rising slowly in the mother-liquor, and finally occupying the upper part of the liquid. Thus it is that the fluid is milky, and that the emulsion takes a much longer time to rise to the surface than pure oil would. The chemical analysis of the emulsion bears out this view, for I have found it to consist invariably of free fatty acid and soap.

This theory may have been already proposed without my knowledge; its adoption will assist in explaining the absorption of fats: for in this case, when in the form of an emulsion, they can no longer be in direct contact with the intestines, a layer of soap intervening between the fat and the membrane. Soaps may be conceived to pass through a membrane, whilst fat is known to be incapable of so doing, consequently we may imagine fats to be absorbed under the form of complex globules, the inside of which is free fat, and the outside soap.

Let us now return to the action of bile upon fats. After I had observed the property of phosphate of soda of emulsioning fatty acid, and not neutral fats, it struck me that bile might be possessed of a similar power, which I found to be the case; and, after giving this important subject all the attention it deserved, the results of my enquiries were communicated to the Royal Society in 1858. Shortly afterwards I was informed that bile had already been observed by Lenz, of Dorpat, to possess the abovementioned property; and, by referring to his valuable Dissertation "On the Digestion of Fats," I found that he was the first who discovered, so far back as 1850, that bile emulsioned fatty acids, but not neutral fats; he also noticed that the emulsion was attended with the formation of soap, and I readily avail myself of this opportunity of acknowledging the fact.

I cannot find that Lenz conducted his experiments with other fats than oil. I employed the solid fats of meat, which are those usually taken into the stomach; my attention was especially directed to the quantitative analysis of the emulsion, in order to determine the proportions of soap and fatty acids it contained; and finally I discovered this remarkable and interesting fact, that if the mother-liquor in which the emulsion is suspended be filtered from the emulsioned fat, it is capable, notwithstanding its strongly acid reaction, of forming more soap and emulsioning more fatty acid, although before filtration the saponification had been entirely arrested; the filtrate from this second operation is likewise capable of effecting a further saponification and emulsion, but the action is less and less powerful; in one series of experiments, the proportions of fatty acids saponified were 20·5 %, 12·7 %, and 3·8 % of those experimented on.

The importance of the change which neutral fats undergo in the stomach will now be readily understood; for it is indispensable to their subsequent emulsion in the intestines by the bile, under which form they are absorbed. I do not wish, however, to attribute to bile exclusively the power of digesting fats: for I fully believe that a portion of the fats taken into the stomach is not acidified, and, consequently, must escape the action of the bile; in this case the pancreatic juice effects the required emulsion. It is remarkable that in both cases the fats are absorbed in great measure under the form of emulsioned fatty acids; for it is now generally admitted that the pancreatic juice has the power of acidifying neutral fats, as was discovered by Prof. Bernard.

This absorption of fatty acids explains a fact I observed, with Mr. Verdeil, while at work in Messrs. Wurtz and Verdeil's laboratory at Paris, in 1851—namely, that blood contains free fatty acids.

The alimentary canal is so perfectly adapted to the functions of digestion, that notwithstanding the great variety of food taken, and the amount of nourishment ingested, which is frequently much greater than that strictly required for the maintenance of the body, only a very small proportion of food passes off in the evacuations in the healthy state; they may be said to contain no element of food soluble in water, for they merely yield to water a small quantity of an albuminous substance possessed of the characters of the albumin of the pancreatic juice, which in all probability it is. Under the microscope, we find in the alvine dejections, a few fragments of muscular tissue, from the meat taken, and the hairs of wheat ingested with bread; a few cells and fibres are all that remains of vegetable food. None of the fats of food are found therein in the free state, but the evacuations contain small quantities of phosphate of soda, soda soaps, and a larger proportion of earthy phosphates and earthy soaps.

The principal object of the alvine evacuation is obviously to rid the body of certain parts of the intestinal secretions, which, after having served their purpose in effecting the digestion of food, are not fit to return into the blood. It is very difficult to trace the connection of these excreted substances with the various intestinal secretions; in this respect, we must at present rest satisfied with probabilities. Among these various substances there is one of great interest, I have called *excretin* [$C_{78}H_{78}O_2S$.]. This substance, which has been fully described elsewhere,* crystallises from its alcoholic or ethereal solution, exhibiting beautiful silky crystals, which are acicular four-sided prisms. In its properties it closely resembles *cholesterin,* being soluble in hot alcohol and ether, sparingly soluble in cold alcohol, insoluble in water, and not saponifiable; like cholesterin, it dissolves in small quantity in the bile. It has also some physiological connection with chlolesterin, as I have found the excreta of very young children to contain no excretin, but chlolesterin, whilst it is the reverse in the case of young people and adults. On this account, I believe excretin to be a constituent of the bile.

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* Phil. Trans., 1854, ii, 265.

L.—*On the Hydrides of the Alcohol-radicles existing in the Products of the Destructive Distillation of Cannel Coal.*

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The light oils produced in the destructive distillation of coal have lately found so extended an application in the arts, that the yield of these oils, in the process of gas-making, has proved quite insufficient to meet the trade demand.

Considerable quantities of coal are, therefore, now distilled with the sole object of obtaining liquid products. The yield of volatile liquid depends, as is well known (1), upon the circumstance that the distillation is conducted at as low a temperature as possible, and (2) that the substances, when once formed, are not decomposed by exposure to a red heat.

Mr. John Barrow, of the Dalton Chemical Works, Gorton, near Manchester, has been kind enough to place a sufficient quantity of the light oils obtained by the distillation of coal at my disposal, to enable me to undertake a thorough examination of their chemical composition. They are obtained by Mr. Barrow, on the large scale by distilling Wigan Cannel in retorts, the lower surfaces of which are heated, whilst the upper parts are kept as cool as possible.

The crude oil possesses the peculiar smell of the compound ammonias, and when these are removed by treating the liquid with dilute sulphuric acid, the oil assumes the peculiar garlic-like smell of the higher olefines.

On submitting the oil to repeated fractional distillation, a small quantity of liquid is obtained boiling below 20° C., a considerable quantity distils between 35°—45° C., much less from 45°—65°, whilst above 65° about equal portions distil for every 5° of increase of temperature. It was, however, found impossible to obtain a product of constant boiling point by repeated fractional distillations.

When concentrated nitric acid is brought in contact with the oil, so violent an oxidation occurs, that spontaneous ignition of the more volatile portions of the oil sometimes takes place. When the action is moderated by cooling, a large portion of the oil remains unacted upon, whilst considerable quantities of nitro-compounds are formed.

I confine myself, in the present communication, to the consideration of the liquids which remain unacted upon by nitric acid, and are contained in the crude oil boiling below 120° C.

The separation of these oils by means of nitric acid is a tedious and disagreeable operation. It may, however, be easily effected by previously shaking up the crude oil with an equal volume of ordinary sulphuric acid. The mixture becomes heated, assumes a dark colour, and gives off a smell resembling that of peppermint, and after some time sulphurous acid is evolved.

The liquids were allowed to remain in contact for several days, and were frequently shaken; the oil was then poured off, washed with water and distilled, a large quantity of tarry matter being left behind in the retort.

The distillate consisted mainly of benzol and toluol, together with the liquids unacted upon by acids. For the purpose of obtaining the latter liquids in the pure state, I have employed the method described by Greville Williams in his researches on the hydrocarbons from Boghead coal.* This method consists in repeatedly shaking the oil with concentrated nitric acid, until, on addition of water to the acid liquid, no further separation of nitro-compounds occurs. The liquid unacted upon is then washed with water, dried over potash, and repeatedly rectified over sodium.

By fractional distillation of this liquid, the following four bodies were obtained—

C_5H_{12}	boiling point	39— 40° C.
C_6H_{14}	,, ...	68— 70° ,,
C_7H_{16}	,, ...	98— 99° ,,
C_8H_{18}	,, ...	119—120° ,,

It will be shown that these liquids are the hydrides of the alcohol-radicles, inasmuch as they have been transformed by the action of chlorine into their corresponding chlorides.

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* Phil. Transact., 1857.

(1) *Hydride of Amyl:* $Ȼ_5H_{12}$.

Analysis: 0·1870 substance gave 0·5715 carbonic acid and 0·2810 water.

	Calculated.		Found.
$Ȼ_5$	60	83·33	83·3
H_{12}	12	16·67	16·7
	72	100·00	100·0

Determination of Vapour-density.

(*a*)	Substance taken	0·1010 grm.
	Temperature of air	16°·0 C.
	Temperature of vapour......	55°·0 C.
	Volume of vapour..........	54°·8 cbc.
	Height of barometer........	752°·0 mm.
	Difference of level	235°·5 mm.

The density calculated from these numbers is 2·523.

(*b*)	Temperature of vapour.... .	66°·0 C.
	Volume of vapour..........	56°·0 cbc.
	Difference of level..........	230°·0 mm.

Hence the vapour-density = 2·519.

(*c*)	Temperature of vapour......	91°·0 C.
	Volume of vapour..........	59°·5 cbc.
	Difference of level..........	220°·0 mm.

These numbers give the density of 2·497, closely corresponding to the theoretical density 2·493 of hydride of amyl.

Hydride of amyl is thin mobile liquid, boiling between 39 and 40° C., and possessing a pleasant smell, resembling that of chloroform. Sp. gr. = 0·636 at 17° C. It burns with a bright, luminous, non-fuliginous flame. These properties, with the exception of the boiling point, correspond with those of the hydride of amyl, as described by Frankland. Although a small portion of the purified oil distils over below 30° C., I did not succeed, after repeated fractional distillations, in obtaining a liquid having a constant boiling of 30° C., as found by Frankland, by far the greatest part of the liquid distilling between 39—40° C.

Greville Williams has lately shown the presence of hydride of amyl in the oils obtained by the destructive distillation of Boghead coal.*

(2) *Hydride of Hexyl* (*Caproyl*) *:* Ꞓ_6H_{14}.

Analysis: 0·1460 substance gave 0·4490 carbonic acid, and 0·2135 water.

	Calculated.		Found.
Ꞓ_6	72	83·72	83·8
H_{14}	14	16·28	16·3
	86	100·0	100·1

Determination of Vapour-density.

Balloon with air	23°·449 grms.
Temperature of air	15°·5 C.
Balloon with vapour..............	23°·720 grms.
Temperature on sealing	110°·0 C.
Capacity of balloon..............	178°·0 cbc.

Hence the vapour-density = 2·98; the theoretical-density of hydride of hexyl is 2·98.

Hydride of hexyl is a thin mobile liquid, of a faint but pleasant smell, burning with a luminous, slightly smoky flame. Boiling point 68—70° C. Sp. gr. at 15°·5 = 0·678.

There can be little doubt that the body, possessing the same composition and boiling point, which Greville Williams found in the oils from Boghead coal, described in his first paper as propyl, is really hydride of hexyl. Cahours and Pelouze have lately shown that it is contained in large quantities in the American rock oil.†

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* Journ. Chem. Soc. xv., 130.

† Phil. Trans., 1857.

3. *Hydride of Heptyl (Oenanthyl)* : $Ȼ_7H_{16}$.

Analysis :—0·1765 substance gave 0·5440 carbonic acid and 0·2570 water.

	Calculated.	Found.
$Ȼ_7$	84·0	84·0
H_{16}	16·0	16·1
	100·0	100·1*

Determination of Vapour-density.

Balloon with air.	24°·368 grms.
Temperature of air.	18°·0 C.
Balloon with vapour	24°·671 grms.
Temperature on sealing	150°·0 C.
Capacity of balloon	179°·0 cbc.
Residual air	0°·3 cbc.

These numbers give the vapour-density . . . . = 3·49
The theoretical density of hydride of heptyl is = 3·46

Hydride of heptyl is a liquid closely resembling hydride of hexyl; it possesses a similar smell, and burns likewise with a slightly smoky flame. Boiling point 98—99° C. Specific gravity at 17·5° = 0·709.

When chlorine is passed into hydride of heptyl, the liquid becomes warm, and hydrochloric acid is given off. The substitution-products formed are partially decomposed by distillation; hydrochloric acid is evolved, and carbon separates out, and the distillates assume green, blue, or purple colours, which disappear after standing for some time. A large portion however of the chlorinated liquid distils without decomposition; and from this portion, when the treatment with chlorine has not been carried too far, a considerable quantity is obtained by fractional distillation, boiling between 150—152° C (not corrected). This body possesses the composition and properties of chloride of heptyl $Ȼ_7H_{15}Cl$.

Analysis: The combustion was effected with oxide of copper, the front part of the tube containing copper-turnings.

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* Compt. rend. liv. 1241.

0·2522 substance gave 0·5765 carbonic acid and 0·2580 water. 0·2032 substance gave 0·2120 chloride of silver and 0·0036 metallic silver.

	Calculated.		Found.
$Ꞓ_7$	84	62·45	62·3
H_{15}	15	11·15	11·4
Cl	35·5	26·40	26·4
	134·5	100·0	100·1

Chloride of heptyl is a colourless liquid, of a pleasant smell, burning with a smoky, green-bordered flame, and possessing the specific gravity of 0·891 at 19° C.

When it is boiled with an alcoholic solution of acetate of potassium, chloride of potassium separates out, but the decomposition goes on very slowly. When, however, the mixture is heated in sealed tubes to about 120—130° C., the chloride is completely decomposed in a few hours, and the liquid consists of an alcoholic solution of acetate of heptyl, which separates out on the addition of water, as a light oily liquid, having a strong and pleasant smell of pears. Treated with an aqueous solution of potash, this ether is easily decomposed and heptylic alcohol is formed, possessing a peculiar aromatic smell, resembling somewhat that of octylic alcohol as prepared from castor oil. I am at present engaged upon the investigation of the heptyl compounds.

Besides the chloride of heptyl, some chlorine-compounds, boiling at higher temperatures and distilling without decomposition, were formed, but the quantity was only small and I did not succeed in obtaining a product of constant boiling point. Heated with sodium, these chlorine-compounds are easily decomposed, and a liquid, free from chlorine is obtained, which boils between 95—100° C., and possesses the peculiar smell of heptylene $Ꞓ_7H_{14}$.

Analysis: 0·1618 substance gave 0·5080 carbonic acid, and 0·2125 water.

	Calculated.		Found.
$Ꞓ_7$	84	85·71	85·6
H_{14}	14	14·29	14·6
	98	100·00	100·2

The quantity obtained was too small for determining the vapour-density.

(4) *Hydride of Octyl (Capryl)* : $Ȼ_8H_{18}$.

Analysis: 0·2095 substance gave 0·6465 carbonic acid and 0·3040 water.

	Calculated.		Found.
$Ȼ_8$	96	84·21	84·1
H_{18}	18	15·79	16·1
	114	100·0	100·2

Determination of Vapour-density.

Balloon with air	7·098 grms.
Temperature of air	15·5° C.
Balloon with vapour..............	7·33 grms.
Temperature on sealing	170·0° C.
Capacity of balloon	119·5 cbc.

The vapour-density calculated from those numbers = 3·98
The theoretical density of Hydride of Octyl is .. = 3·95

Hydride of octyl in its physical properties closely resembles the hydrides of hexyl and heptyl. It boils at 119—120°, and has a spec. grav. of 0·719 at 17°·5.

In the above-mentioned paper on the hydrocarbons from the oil obtained by the destructive distillation of Boghead coal, Greville Williams has described as butyl, a body of the above composition and boiling point, which is doubtless hydride of octyl.

The action of chlorine on hydride of octyl is similar to the action on hydride of heptyl; a large portion of the products formed are decomposed when distilled; whilst the portion which volatilizes without decomposition, yields by fractional distillation a considerable quantity of a liquid boiling between 170—172° C. (not corrected), which possesses the composition and properties of chloride of octyl $Ȼ_8H_{17}Cl$.

Analysis: I. 0·1800 substance, gave 0·4250 carbonic acid, and 0·1895 water.

II. 0·1697 substance, gave 1635 chloride of silver, and 0·0015 metallic silver.

Analysis: III. 0·2342 substance, gave 0·2280 chloride of silver, and 0·0012 metallic silver.

	Calculated.		Found.		
			I.	II.	III.
C_8	96	64·65	64·4	—	—
H_{17}	17	11·45	11·7	—	—
Cl	35·5	23·90	—	23·9	24·2
	148·5	100·0			

Chloride of octyl is a colourless liquid, possessing a faint but pleasant smell of oranges, and burning with a smoky, green-bordered flame. Spec. grav. = 0·892,* at 18° C.

Heated with an alcoholic solution of acetate of potassium, it is decomposed in the same manner as chloride of heptyl.

The volatile chlorine-compounds which are formed together with chloride of octyl, were present in small quantity only, and I was unable to obtain a product of constant boiling point. Heated with sodium, they are easily decomposed, and I observed the formation of the blue body described by Bouis.† By repeated treatment with sodium at a higher temperature, a liquid, having a smell like that of heptylene, was obtained, boiling between 115—125° C. By fractional distillation, the greatest portion was obtained between 115—117° C. Bouis gives the boiling point of octylene at 125° C.

The analysis of the liquid boiling at 115—117° C. gave the following results:—

Substance taken..........	0·1394
Carbonic acid obtained....	0·4375
Water obtained..........	0·1845

	Calculated.		Found.
$Ȼ_8$	96	85·71	85·6
H_{16}	16	14·29	14·7
	112	100·00	100·3

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* It appears from a number of determinations, that the spec. grav. of $Ȼ_7H_{15}Cl$ and $C_8H_{17}Cl$ are very nearly the same.

† Compt. rend xxxviii. 935.

Determination of Vapour-density.

Balloon with air	8°·0015 grms.
Temperature of air	18°·5 C.
Balloon with vapour..............	8°·1080 grms.
Temperature on sealing	177° C.
Capacity of balloon..............	51°·7 cbc.

The density calculated from these numbers is .... 4·17,
whilst the theoretical density of octylene is .... 3·88.

I have convinced myself that the oils from Cannel coal, having a higher boiling point than those I have as yet examined, likewise contain substances unalterable by the strongest acids. There appears therefore to be little doubt that the whole series of homologous hydrides are contained in the products of the distillation of coal at low temperatures; and I would venture the suggestion that the so-called paraffins, which are likewise not acted upon by strong acids, may prove to be the higher members of the same series.

In conclusion, I beg to express my best thanks to Professor Roscoe for the valuable advice which he has given me in carrying out the above investigation.

LI.—*On Capillary Liquid Transpiration in relation to Chemical Composition.*

By Thomas Graham, F.R.S., Master of the Mint.

[From the Philosophical Transactions, 1862.]

The passage of liquids under pressure through a capillary tube is here spoken of as capillary liquid transpiration, in accordance with the analogy of gaseous transpiration. The subject owes the development which it has already acquired chiefly to the investigations of the late Dr. Poiseuille.* The precision of the results attainable by the mode of experimenting pursued by that physicist has been remarked on by every one who has followed him in the inquiry. The observations on this subject which we owe to M. Poiseuille and other inquirers are very numerous, but have not, so far as I am aware, been connected hitherto with any speculative views of the chemical or molecular constitution of liquids.

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* Mém. Savans Etrangers, ix., 433; Ann. Ch. Phys. [3], vii. and xxi.

The isolated discovery of M. Poiseuille, that diluted alcohol has a point of maximum retardation, coinciding with the degree of dilution at which the greatest condensation of the mixed liquids occurs, appears to offer a starting point for new inquiries. The same result may be otherwise expressed, by saying that the definite compound of 1 equivalent of alcohol with 6 equivalents of water, $C_4H_6O_2+6HO$*, is more retarded than alcohol containing either a greater or a smaller proportion of water. The rate of transpiration appears here to depend upon chemical composition, and to afford an indication of it. A new physical property may thus become available for the determination of the chemical constitution of substances. Methylic alcohol being found to exhibit the same remarkable feature in its transpiration, although the 6-hydrate of that alcohol is not distinguished by extraordinary condensation of volume, the inquiry was extended to the hydrated acids. The results obtained with the latter substances give a certain degree of generality to the relation subsisting between the transpirability and chemical composition of liquids.

The apparatus employed was very similar to that of M. Poiseuille. It consisted of a small but rather stout glass bulb, A (see figure), about two-thirds of an inch in diameter, having a capacity of from 4 to 8 cub. cent., blown upon a thick glass tube, with a bore of about 2 millimetres. A scratch (*c*) was made upon the glass tube above, and another (*d*) below the bulb, to indicate the available capacity of the instrument. The lower tube was bent at a right angle to the upper, and a fine capillary tube, B, from 3 to 4 inches in length, was sealed to the curved extremity of the tube. The bulb and capillary were always held immersed in a vessel of water during the experiment, in order to secure uniformity of temperature. The force employed to impel the liquid through the capillary was the weight of one atmosphere of

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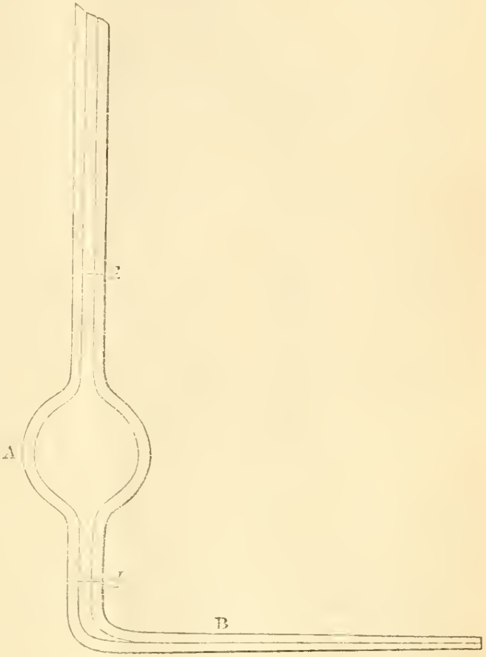
* Halving the equivalent of alcohol, the hydrate of greatest retardation becomes $C_2H_3O + 3HO$.

760 millimetres of mercury, and was obtained from compressed air contained in a large reservoir provided with a mercurial gauge, as in Poiseuille's experiments. The time was noted in seconds which the level of the liquid in the bulb took to fall from the mark *c* to the mark *d*. This time varied from about 300 to 900 seconds in different liquids. In successive experiments made upon the same liquid, the variation in the time, or error of observation, did not exceed one or two seconds. The experiment was always repeated two or three times, and a mean taken. The temperature of the liquid transpired was always 20° C. (68° F.), when not otherwise stated.



The liquid may be introduced into the bulb through the open upper tube by means of a tube-funnel; but it was found more convenient in practice, although requiring a much longer time, to fill the bulb by aspiration through the capillary. With this view, the compressed air was shut off by a stop-cock, and the upper tube of the bulb was then allowed to communicate with the receiver of an air-pump, instead, by which exhaustion was produced, while the open end of the capillary was immersed in a portion of the liquid. The liquid which entered the bulb in this manner was sure to be free from any solid matter that could cause obstruction in the capillary during the subsequent passage of the liquid outwards, while the disconnecting of the bulb from the rest of the apparatus, for the purpose of filling the former, was also avoided.

Nitric Acid.

A bulb provided with a capillary tube, distinguished as capillary C, was used in the transpiration of nitric acid and of several other liquids. The dimensions of this bulb C were as follows:— Capacity of bulb, 8·075 cub. cent.; length of capillary tube, 28 millims.; diameter of bore, 0·0942 millim. The time of passage of water through the tube, under the pressure of one atmosphere and at the fixed temperature of 20°, was 348 seconds. The time of the passage of the most highly concentrated nitric acid through the same capillary was found to be 344·5 seconds, or slightly less than the time of water. This is the protohydrate of nitric acid, $HO.NO_5$ or NHO_6. With the addition of water to the acid, the transpiration of equal volumes of liquid becomes gradually slower; till as much as three additional equivalents of water were added, when the transpiration-time rose to its maximum, 732 seconds. The last hydrate is the well-known definite compound $NHO_6 + 3HO$, having the specific gravity 1·4, and possessing the highest boiling point of any compound of nitric acid and water. Diluted beyond this point, nitric acid begins to pass more freely, and the transpiration-time approaches again to that of water. With the addition of twice its weight of water, or about 7 equivalents, the acid passed through the capillary in 472 seconds.

The experiments made upon nitric acid are recorded in the following Table. It will be observed that the retardation is considerable for a certain distance on both sides of the maximum point. No unusual retardation appears to occur with the proportions of water corresponding to 2 and 4 equivalents. The specific gravity of the acid liquid is added in the last column of the Table, whenever that property was observed.

Table I.—Transpiration of Nitric Acid, at 20° C., by Capillary C.*

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (NHO_6).	Water, per cent.	Transpiration-time.		Spec. grv. at 15°.
		In seconds.	Water = 1.	
0	0	344·5	0·9899	1·5046
25·47	20·38	692	1·9885	1·4358
28·56 .. 2 eqs. HO	21·43	705	2·0258	
30	23·07	712	2·0459	
40	28·50	725	2·0833	
42·85 .. 3 eqs. HO	29·99	732	2·1034	1·3978
45	31·03	730	2·0977	
50	33·33	728·5	2·0919	1·3816
55	35·48	718	2·0632	
57·12 .. 4 eqs. HO	36·35	712	2·0459	
60	37·50	709·5	2·0387	1·3598
70	41·17	683	1·9626	1·3407
80	44·44	661	1·8994	1·3239
90	47·36	635·5	1·8261	
100	50·00	593	1·7040	1·2943
200	66·66	472	1·3563	

It appears then, that a certain hydrate of nitric acid is marked out by its low transpirability so distinctly, that nitric acid could be identified by that physical property. Such a property may prove to be typical of a class of acids to which nitric acid belongs. The hydration of nitric acid probably advances by three equivalents at a time, NHO_6+3HO, as in the magnesian nitrates, $NMO_6+3HO+3HO$. The transpiration of the assumed second hydrate of nitric acid was not made the subject of experiment. A certain steadiness is observed in the transpiration of this acid on either side of the point of maximum retardation.

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* In the following tables, the particular capillary employed is in each case designated by a particular letter. Capillary C, which was more employed than any other, became reduced in length during the course of the experiments, the end being ground off on several occasions on account of the choking of the tube. This capillary is then described as C shortened. It did not seem requisite to give in every case the dimensions of the bulb and capillary tube, as all the experiments were conducted on the same plan, and the transpiration of water is in every case given as a standard of comparison. Direct experiments were also made, which proved that the transpiration-times were sensibly inversely proportional to the effective pressure applied to the liquid, as found by Poiseuille; which indicates that the capillaries offered sufficient resistance to the passage of the liquid.

Sulphuric Acid.

Table II.—Transpiration of Sulphuric Acid, at 20°, by Capillary G.

(Transpiration-time of water, 109 seconds.)

Water added to 100 acid (SHO_4).	Water, per cent.	Transpiration-time.		Spec. grv. at 15°.
		In seconds.	Water = 1.	
0	0	2360	21·6514	1·8456
2·5	2·43	2412	22·1284	1·8398
5	4·76	2451	22·4862	1·8346
10	9·09	2516	23·0825	1·8120
12·5	11·11	2548	23·3761	1·7976
15	13·04	2587	23.7340	1·7800
17·5	14·89	2591	23·7706	
18·36 .. 1 eq. HO	15·13	2466	22·6238	1·7590
20	16·66	2398	22·0000	1·7473
30	23·07	1523	13·9724	1·6700
36·73 .. 2 eqs. HO	26·86	1189	10·9090	1·6335
40	28·50	1056	9·6880	1·6146
50	33·33	810	7·4302	1·5600
60	37·50	626	5·7431	1·5118
70	41·17	535	4·9082	
80	44·44	450	4·1284	
100	50·00	382	3·5045	
120	54·54	332	3·0458	
140	58·33	290	2·6605	
160	61·53	260	2·3889	
180	64·28	241	2·2110	
200	66·66	227	2·0825	

The transpiration of sulphuric acid is very slow, being-twenty-four times less rapid than that of water, as might be expected from the viscous quality of the acid fluid. It is surprising, however, that the first additions of water do not promote the transpiration, although they lessen in a sensible degree the viscosity of the liquid. The transpiration-time increases from 2,360 to 2,591 seconds, and then attains the maximum, when 17·5 parts of water have been added to 100 parts of oil of vitriol. The proportion of water named approaches closely to one equivalent (18·36 parts). Indeed it is quite possible that the acid mixture which exhibits the least transpirability might have contained a full equivalent of water, for a portion of aqueous vapour may have been absorbed from the air during the process of filling the bulb. That the crystallisable hydrate of sulphuric acid, $SHO_4 + HO$, is the liquid of least transpirability is, I believe, the proper inference from these observations. With increasing proportions of water, the transpiration-time rapidly diminishes, till the time is reduced to 227 seconds in a mixture of oil of vitriol with twice its weight of water.

A more minute examination than has been attempted would be required to show whether the existence of other definite hydrates of sulphuric acid may be indicated by a perceptible retardation in the time of transpiration.

Acetic Acid.

TABLE III.—Transpiration of Acetic Acid, at 20°, by Capillary C.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid ($C_4H_4O_4$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0·8	0·8	445·5	1·2801	
15 .. 1 eq. HO	13·04	890	2·5574	1·0735
20	16·66	921·5	2·6480	1·0742
25	20·00	931	2·6753	
27·5	21·56	933	2·6810	
30 .. 2 eqs. HO	23·07	941	2·7040	1·0752
32·5	24·52	934	2·6839	1·0746
35	25·92	928	2·6666	
40	28·50	912	2·6207	
45	31·04	895	2·5718	
50	33·33	882	2·5344	1·0720
60 .. 4 eqs. HO	37·50	852	2·4482	1·0700
90 .. 6 eqs. HO	47·36	769	2·2098	

The glacial acetic acid made use of in these experiments still retained 0·8 per cent. of water. Its transpiration-time was 445·5 seconds. With the addition of 1 equivalent of water, the time rose to 890 seconds; and with 2 equivalents of water, to 941 seconds, when it attained its maximum. This last is the characteristic hydrate of acetic acid, $C_4H_4O_4 + 2HO$. It is marked out with great precision in these transpiration experiments. The times rise very gradually on either side, and appear to culminate exactly at that point. It is also the compound of water and acetic acid of maximum density, as is well-known. The transpiration-time of the hydrate referred to is so much as 2·7 times longer than that of pure water. With 6 equivalents of water, acetic acid is still transpired 2·2 times more slowly than water.

Butyric Acid.

TABLE IV.—Transpiration of Butyric Acid, $C_8H_8O_4$, at 20°, by Capillary C shortened.

Transpiration-time of water, 290 seconds.)

Water added to 100 acid ($C_8H_8O_4$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	454	1·565	·9740
10·22 .. 1 eq. HO	9·27	828	2·855	·9901
20·45 .. 2 eqs. HO	16 98	951	3·279	·9975
30·67 .. 3 eqs. HO	23·47	969	3·341	
38·69 .. 4·8 eqs. HO	27·85	863	2·975	

In transpirability of its hydrates, burytic acid presents a considerable analogy to acetic acid, as might be expected from the rotation of these acids in composition. The time of the acid ($C_8H_8O_4$) is 1·565, referred to that of water as 1, and it rises to 2·855 by the addition of 1 equivalent of water. By a second equivalent of water, the time is increased to 3·279. Here, however, the progression does not immediately turn, as with acetic acid, but the time rises to 3·341 with 3 equivalents of water. With 3·8 equivalents of water the time is 2·975, and has accordingly very sensibly receded, the maximum point being passed. It is conceivable that the relation to acetic acid is slightly modified in butyric acid by the interference of some other physical property, such as unctuosity, that is unequally developed in the two acids.

Valerianic Acid.

The hydration of this acid cannot be carried beyond 2 equivalents, but up to that point the transpiration is retarded by every addition of water, as in acetic and butyric acids. While the basic hydrate ($C_{10}H_{10}O_4$) is transpired in 2·155 times the water period, the time increases to 3·634 with 1 equivalent of water added, and to 3·839 with 2 equivalents.

TABLE V.—Transpiration of Valerianic Acid, at 20°C, by Capillary C shortened.

(Transpiration-time of water, 290 seconds.)

Water added to 100 acid ($C_{10}H_{10}O_4$).	Water, per cent.	Transpiration.time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	625·2	2·155	·9350
8·82 .. 1 eq. HO	8·10	1054	3·634	·9484
17·64 .. 2 eq. HO	15·84	1113·5	3·839	·9519

Formic Acid.

Formic acid appears to diverge considerably from the other members of the acetic acid series in certain physical and chemical characters. While the acetic hydrate is lighter than water, and is increased in density by the addition of water, the formic hydrate has a higher density than water, and has its density uniformly lowered by dilution, as will be seen in the Table which follows. The transpiration-time of formic acid, in a concentrated state, is also highest, and diminishes with dilution in the same regular manner as the density, showing no evidence of the acetic maximum at the point of 2 equivalents of water. Indeed, formic acid does not appear to affect that particular degree of hydration so characteristic of the acetic acid series. Hence it is, also, that we have no subformate of lead corresponding with the subacetate of lead, and have occasion to remark a general absence of basic formates. The physical properties of liquid formic acid are more suggestive of hydrochloric acid than they are of acetic acid.

The most concentrated formic acid that could be prepared still contained 3·6 per cent. of water. The transpiration-time of that liquid, it will be seen, is 1·718 referred to water as 1; and of the 2-hydrate 1·486. There is evidence of retardation between the points of 3 and 4 equivalents of water, but it is difficult to say with which of these two hydrates the retardation should be connected. More numerous and minute observations would be required to settle the point. We can only draw the negative conclusion from the Table, that the maximum retardation does not coincide with the 2-hydrate as in acetic acid.

TABLE VI.—Transpiration of Formic Acid, at 20°, by Capillary C shortened.

(Transpiration-time of water, 293 seconds.)

Water added to 100 acid ($C_2H_2O_4$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
3·73	3·6	503·5	1·718	1·2265
19·56 .. 1 eq.	16·35	484·5	1·653	1·2019
39·13 .. 2 eqs.	20·93	435·5	1·486	1·1765
58·69 .. 3 eqs.	36·98	411	1·402	1·1524
68·47 .. 3·5 eqs.	40·64	401·5	1·368	1·1466
78·26 .. 4 eqs.	43·90	402·5	1·372	1·1408
97·82 .. 5 eqs.	49·44	388·5	1·325	1·1275
117·35 .. 6 eqs.	53·99	376·5	1·284	1·1203
136·95 .. 7 eqs.	57·79	359	1·225	1·1062

Hydrochloric Acid.

The most concentrated form of this acid that was dealt with, acid of sp. gr. 1·1553, contained already upwards of 8 equivalents of water. Its transpiration-time was 1·736, referred to the time of water as 1. With further dilution, the time diminished, till at the proportion of 12 equivalents of water the time had fallen to 1·5287. About this point, the rate of diminution is reduced, and the transpiration-time even becomes stationary for a short portion of the range of hydration. The retardation observed appears to coincide with the formation of a 12-hydrate of hydrochloric acid. The existence of such a compound is further supported by the fact that solutions of hydrochloric acid tend to the same composition by evaporation at the atmospheric temperature. The degree of hydration of most stability at high temperatures, and having the highest boiling-point, is known to be at or near the proportion of the 16-hydrate. The existence, however, of the latter hydrate, at the ordinary temperature, is not supported by the transpiration experiments now recorded, conducted as these were at a low temperature.

Table VII.—Transpiration of Hydrochloric Acid, at 20°, by Capillary C.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (HCl).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
221·8	69·23	604	1·7356	1·1553
250	71·42	569	1·6336	1·1411
280	73·67	536	1·5404	1·1303
290	74·36	532	1·5287	
295·89 .. 12 eqs. HO	74·74	532	1·5287	1·1246
300	75·00	520	1·4942	
310	75·60	516	1·4827	1·1202
380	79·20	486	1·3965	1·1021
394 .. 16 eqs. HC	79·97	479	1·3764	1·0992
310	80·39	469	1·3476	1·0961

Alcohol.

The fundamental discovery made by Poiseuille of a point of maximum retardation in the transpiration of diluted alcohol is fully confirmed in the following series of observations. The transpiration-time rises from that of absolute alcohol, 1·1957 (water being 1), to 2·7872, when the alcohol is united with 6 equivalents of water, and then falls off again by further additions of water.

Table VIII.—Transpiration of Alcohol, at 20°, by Capillary D.

(Transpiration-time of water, 470 seconds.)

Water added to 100 Alcohol.	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	562	1·1957	
1	0·99	578	1·2297	·7069
3	2·91	615	1·3085	·8030
5	4·76	650	1·3829	·8083
7	6·54	695	1·4787	
10	9·09	734	1·5617	
20	16·66	851	1·8106	·8396
30	23·07	950	2·0212	·8557

TABLE VIII.—continued—

Water added to 100 Alcohol.	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
40	28·50	1029	2·1893	·8683
50	33·33	1093	2·3253	·8800
60	37·50	1152	2·4510	·8897
70	41·17	1213	2·5808	·8983
72·5	42·02	1230	2·6170	·9003
75	42·85	1231	2·6191	·9021
78·26 .. 4 eqs. HO	43·94	1239	2·6361	·9045
80	44·44	1238	2·6340	·9058
82·5	45·20	1242	2·6425	·9073
85	45·94	1244	2·6468	·9088
90	47·36	1256	2·6723	·9120
100	50·00	1268	2·6978	·9183
110	52·38	1282	2·7276	·9235
112·5	52·94	1287	2·7382	·9249
115	53·49	1298	2·7617	·9255
117·39 .. 6 eqs. HO	54·04	1310	2·7872	·9271
120	54·54	1307	2·7808	·9288
122	55·05	1300	2·7659	·9292
125	55·55	1297	2·7595	·9304
130	56·52	1297	2·7595	·9328
140	58·33	1295	2·7553	·9363
150	60·00	1280	2·7234	·9396
160	61·53	1255	2·6702	·9430
170	62·92	1250	2·6505	·9451
180	64·28	1246	2·6510	·9482
190	65·51	1240	2·6382	·9500
200	66·66	1235	2·6276	·9521
250	71·42	1165	2·4787	·9601
300	75·00	1094	2·3276	·9652
350	77·77	1026	2·1829	·9689
400	80·00	973	2·0702	·9716
450	81·80	934	1·9872	·9738
500	83·33	908	1·9319	·9759

It will be observed that, after attaining its maximum, the transpiration-time falls off in a very gradual manner, till at least another equivalent of water has been added. With still further dilution, the shortening of the transpiration-time is considerably more rapid. The Table appears to indicate a slight retardation at the proportion of four equivalents of water; but this would require confirmation. It is remarkable that hydrated liquid compounds appear in general to show only one decided transpiration maximum, as with the 1-hydrate in sulphuric acid, the 2-hydrate in acetic acid, the 3-hydrate in nitric acid, the 6-hydrate in alcohol, and the 12-hydrate in hydrochloric acid.

A considerable number of experiments were made upon specimens of *methylic alcohol* prepared at different times, with some discrepancy in the results. Although always derived from crystallized methylic oxalic ether, the liquid varied sensibly in transpirability. As the cause of this variation has not yet been ascertained, I shall confine myself at present to one statement, namely, that a particular specimen of methylic alcohol gave 0·63 as the transpiration-time of the anhydrous substance (water being 1), and 1·8021 as the time of the 6-hydrate, $C_2H_4O_2+6HO$, and that for a considerable distance on either side of that point of hydration, the transpiration was slightly less and nearly constant, as it is in vinic alcohol. It may be inferred, therefore, with some probability, that alcohols have a maximum of retardation at the same stage of dilution.

Three alcohols in a state of purity were transpired through the same capillary, with water for comparison, at 20°. The time of water was 297 seconds.

TABLE IX.—Transpiration of Alcohols, at 20°.

	Transpiration-time.		Spec. grav. at 15°.	Boiling-point.
	In seconds.	Water = 1.		
Methylic alcohol	187·25	0·630	·7973	66° C.
Vinic alcohol	355·1	1·195	·7947	78·5
Amylic alcohol	1084	3·649	·8204	132

It will be remarked that the transpiration-time of an alcohol increases with the elevation of its temperature of ebullition. A similar observation applies to the transpiration of ethers.

TABLE X.—Transpiration of Ethers, at 20°, by Capillary C shortened. (Transpiration-time of water, 290 seconds.)

	Transpiration-time.		Spec. grav. at 15°.	Boiling-point.
	In seconds.	Water = 1.		
Formate of ethyl	148·2	0·511	·9174	55°·5
Acetate of ethyl	160·5	0·553	·8853	74
Butyrate of ethyl	217·5	0·750	·8490	114
Valerate of ethyl	237·5	0·827	·8750	133·5

The transpiration-times of the homologous acids, previously observed, appear also to follow in progression.

Transpiration of Acids, at 20°.

	Acid.	Acid + 2HO.
Acetic acid	1·2801	2·740
Butyric acid	1·565	3·279
Valerianic acid	2·155	3·839

The increase of the transpiration-time of an alcohol, ether, and acid, as each rises in its series, may be connected with the increasing weight of their molecule.

Acetone.

The transpiration of this liquid is remarkably rapid. It is also greatly retarded by the addition of water. The time will be found to rise from 0·401, that of anhydrous acetone, to 1·604, the time of the 12-hydrate, taking the equivalent of acetone as $C_6H_6O_2$, or of the 6-hydrate with the equivalent C_3H_3O.

TABLE XI.—Transpiration of Acetone, at 20°, by Capillary C. (Transpiration-time of water, 348 seconds.)

Water added to 100 acetone ($C_6H_6O_2$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	139·6	0·401	·7943
15·51 .. 1 eq.	13·42	212·5	0·610	·8384
31·03 .. 2 eqs.	23·68	283·5	0·814	·8604
46·55 .. 3 „	31·76	355·5	1·021	·8850
62·06 .. 4 „	38·29	457	1·313	·8990
77·58 .. 5 „	43·68	464	1·333	·9123
85·34 .. 5·5 „	46·04	469	1·347	·9173
93·10 .. 6 „	48·21	482	1·385	·9219
100	50·00	500	1·436	·9251
108·61 .. 7 „	52·06	515·5	1·479	·9300
124·13 .. 8 „	55·33	531·5	1·527	·9320
139·65 .. 9 „	57·85	537·7	1·543	·9413
155·16 .. 10 „	60·81	552·7	1·586	·9468
170·67 .. 11 „	63·05	555·5	1·594	·9504
186·18 .. 12 „	65·05	558·5	1·604	·9526
201·71 .. 13 „	66·85	556·5	1·599	·9563
217·24 .. 14 „	68·41	557	1·600	·9588
232·75 .. 15 „	69·94	553·5	1·590	·9608
248·27 .. 16 „	71·28	549	1·577	·9632
263·79 .. 17 „	72·23	547	1·571	·9649
279·31 .. 18 „	73·63	546	1·568	·9662
294·82 .. 19 „	74·67	539·5	1·550	·9676
372·24 .. 24 „	78·82	519	1·491	·9736

The transpiration-time of acetone attains a maximum at what is represented in the Table as the compound with 12 equivalents of water. The time is nearly stationary for some distance on either side of that point, the range from 10 to 15 equivalents of water being 1·586 to 1·590, with 1·604 as a maximum for the intermediate twelfth equivalent.

Glycerin.

This liquid is too viscid in a state of purity to be transpired by means of the bulb and capillaries employed in these experiments. The observations to be recorded were confined to diluted solutions of glycerin approaching in composition to the 18-hydrate, $C_8H_8O_6 + 18HO$. It was imagined that glycerin, as a triatomic alcohol, might affect combination with water in the proportion named.

TABLE XII.—Transpiration of Glycerin, at 20°, by Capillary C.

(Transpiration-time of water at the same temperature, 348 seconds.)

Water added to 100 Glycerin ($C_6H_8O_6$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
170	62·96	1190	3·445	1·1010
176·07 .. 18 eqs.	63·77	1160	3·333	1·0980
180	64·28	1131·5	3·251	1·0960
190	65·51	1068·5	3·070	1·0934
192	65·75	1054	3·031	1·0927
195	66·10	1049	3·014	1·0914
197	66·32	1039	2·977	1·0912
200	66·66	1026	2·948	1·0905

The transpiration-time of the 18-hydrate is 3·333, referred to water as 1. There is no indication of a maximum at that point, but the numbers descend according to their place in the Table without any interruption.

The idea having suggested itself that the viscous property of glycerin-solutions might overpower or conceal the expected deviation, the transpiration was repeated at a higher temperature, when the solutions possess greater fluidity.

TABLE XIII.—Transpiration of Glycerin, at 60°, by Capillary C. (Transpiration-time of water at the same temperature, 186 seconds.)

Water added to 100 Glycerin ($C_6H_8O_6$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
170	62·96	435·5	2·341	1·1010
172·5	63·30	432	2·322	1·0999
175	63·63	428	2·301	1·0980
176·08 .. 18 eqs.	63·77	425	2·284	1·0976
177	63·96	422·5	2·271	1·0970
180	64·22	420	2·258	1·0960

Still no retardation appears at the point of 18 equivalents, but the time continues to shorten as the proportion of water is increased, according to a pretty uniform progression. The information respecting the constitution of glycerin which transpiration affords is therefore of a negative character.

The existence of a relation between the transpirability of liquids and their chemical composition appears to be established. It is a relation analogous in character to that subsisting between the boiling-point and composition, so well defined by Hermann Kopp. Perhaps the most interesting part of the present subject to develop would be the transpiration of homologous series of substances. Judging from the limited observations on the alcohols, ethers, and acids, the order of succession of individual substances in any series would be indicated by the degree of transpirability of these substances, as clearly as it is by their comparative volatility. In carrying out the inquiry, it would probably be found advantageous to operate at a fixed and somewhat elevated temperature. A large number of substances are liquid at 100°, of which the transpiration-time could be easily obtained.

In hydrated substances, transpiration also affords a manifestation of definite combination at once striking and precise. I need only refer to the manner in which the "constitutional" hydrate of sulphuric acid $SHO_4 + HO$, of acetic acid $C_4H_4O_4 + 2HO$, of nitric acid $NHO_6 + 3HO$, and of alcohol $C_4H_6O_2 + 6HO$ is each indicated by its maximum transpiration-time. The indication of the alcohol-hydrate is particularly distinct, although that hydrate must be a comparatively feeble compound. Indeed the extent to which transpiration is affected by the annexation of constitutional water appears to be by no means in proportion to the intensity of combination.

The increased resistance to transpiration observed in these definite hydrates may be connected with their larger molecules. But another speculative view of the retardation can be suggested, in which the phenomenon is referred to a physical agency. When one of these definite hydrates, say the 6-hydrate of alcohol, is being forced through the capillary, it may be imagined that a small portion of the hydrated compound is molecularily decomposed by the friction. A certain portion of the impelling force would thereby be lost, being converted into the latent heat which alcohol and water require to assume when separated from each other, and the transpiration be consequently retarded; for as alcohol and water evolve heat on combining, so they must absorb heat when their union is dissolved by any cause. But the change of temperature representing the lost force appears to be too small to be rendered sensible to observation. It would be capable of raising the temperature of the transpired liquid not more than about one forty-third part of a degree, according to an accurate estimate for which I am indebted to Professor Stokes. In consequence of this circumstance, the physical hypothesis now suggested has neither been verified nor disproved.

To this paper are appended two series of observations made on transpiration at different temperatures, the first series being the transpiration of water, and the second that of absolute alcohol. Each series of experiments is repeated with two capillary tubes, one having nearly double the resistance of the other. The numbers from the two capillaries exhibit a fair amount of agreement. The times given are those actually observed, no correction being made for the small variation of the capillary in diameter at different temperatures.

The dimensions of Capillary D were as follows:—Capacity of bulb, 4·135 cub. cent.; length of capillary tube, 37·5 millims.; diameter of bore, 0·10325 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 470 seconds.

The dimensions of Capillary E were as follows:—Capacity of bulb, 3·725 cub. cent.; length of capillary, 53 millims.; diameter of bore, 0·0858 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 913 seconds.

TABLE XV.—Transpiration of Alcohol at different Temperatures.

Temperature.	By capillary tube D.					By capillary tube E.				
	Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.		Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.	
		Time.	Velocity.	Time.	Velocity.		Time.	Velocity.	Time.	Velocity.
0°C.	860	1·8297	0·5465	1·0238	0·9767	1642	1·7984	0·5560	1·0079	0·9920
1	840	1·7893	0·5588	1·0012	0·9988	1601	1·7535	0·5702	0·9828	1·0174
3	607	1·7170	0·5824	0·9607	1·0409	1537	1·6834	0·5940	0·9435	1·0598
5	772	1·6425	0·6089	0·9190	1·0880	1473	1·6134	0·6198	0·9042	1·1059
7	738	1·5702	0·6368	0·8785	1·1382	1410	1·5443	0·6475	0·8656	1·1553
10	700	1·4893	0·6714	0·8333	1·2000	1350	1·4786	0·6755	0·8226	1·2066
15	624	1·3276	0·7532	0·7428	1·3461	1213	1·3285	0·7526	0·7446	1·3429
20	562	1·1957	0·8362	0·6690	1·4946	1092	1·1960	0·8360	0·6703	1·4917
25	520	1·1063	0·9038	0·6190	1·6154	1001	1·0963	0·9120	0·6145	1·6273
30	476	1·0127	0·9873	0·5566	1·7646	915	1·0022	0·9978	0·5617	1·7803
35	428	0·9106	1·0981	0·5095	1·9626	843	0·9233	1·0830	0·5175	1·9323
40	391	0·8319	1·2020	0·4654	2·1483	772	0·8455	1·1826	0·4739	2·1101
45	360	0·7659	1·3055	0·4285	2·3333	707	0·7743	1·2913	0·4340	2·3041
50	331·5	0·7053	1·4177	0·3946	2·5339	645	0·7064	1·4155	0·3959	2·5100
55	307	0·6531	1·5309	0·3654	2·7301	592	0·6484	1·5422	0·3634	2·7517
60	285	0·6063	1·6491	0·3392	2·9373	551	0·6035	1·6569	0·3382	2·9564
65	262	0·5574	1·8005	0·3119	3·2061	510	0·5585	1·7901	0·3130	3·1941
70	241	0·5127	1·9502	0·2869	3·4854	468	0·5125	1·9465	0·2873	3·4807

Table XIV.—Transpiration of Water at different Temperatures.

Temperature.	By capillary tube D.					By capillary tube E.				
	Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.		Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.	
		Time.	Velocity.	Time.	Velocity.		Time.	Velocity.	Time.	Velocity.
0°	840	1·7872	0·5593	1·	1·	1629	1·7872	0·5604	1·	1·
1	792	1·6851	0·5934	0·9428	1·0606	1568	1·7174	0·5829	0·9625	1·0389
2	770·5	1·6391	0·6099	0·9172	1·	1514	1·6582	0·6050	0·9294	1·
3	749	1·5936	0·6275	0·8917	1·1216	1461	1·6002	0·6249	0·8975	1·1449
4	727	1·5468	0·6465	0·8654	1·					
5	709	1·5085	0·6629	0·8440	1·1857	1382	1·5136	0·6606	0·8483	1·1787
7	669	1·4234	0·7025	0·7964	1·2556	1289	1·4118	0·7083	0·7912	1·2638
10	618	1·3148	0·7605	0·7357	1·3592	1188	1·3012	0·7685	0·7293	1·3717
14	548	1·1659	0·8576	0·6423	1·5328					
15	533	1·1340	0·8818	0·6345	1·5759	1037	1·1358	0·8804	0·6366	1·5709
16	521	1·1085	0·9021	0·6202	1·6122					
20	470	1·	1·	0·5595	1·7872	913	1·	1·	0·5604	1·7842
25	414	0·8808	1·1352	0·4928	2·0189	823	0·9014	1·0904	0·5052	1·9793
30	375·5	0·7989	1·2516	0·4470	2·2371	743	0·8138	1·2288	0·4501	2·1924
35	338	0·7191	1·3905	0·4023	2·4852	670	0·7338	1·3626	0·4113	2·4313
40	309·5	0·6508	1·5185	0·3684	2·7108	602	0·6593	1·5166	0·3695	2·7059
45	284·5	0·6053	1·6520	0·3386	2·9525	553	0·6056	1·6509	0·3394	2·9459
50	261	0·5553	1·8007	0·3107	3·2184	505	0·5531	1·8079	0·3100	3·2257
55	243	0·5170	1·9341	0·2892	3·4979	475	0·5202	1·9221	0·2916	3·4294
60	228	0·4851	2·0614	0·2714	3·6842	438	0·4797	2·0844	0·2689	3·7191
65	214	0·4553	2·1967	0·2547	3·9252	400	0·4381	2·2825	0·2455	4·0725
70	200	0·4155	2·3500	0·2380	4·2000	378	0·4140	2·4153	0·2321	4·3122

LII.—*On the Chemistry of Opium.*

[A Discourse delivered to the Fellows of the Chemical Society, May 1st, 1862.]

By THOMAS ANDERSON, M.D., F.R.S.E., Professor of Chemistry in the University of Glasgow.

THE chemical history of opium may be said to have its origin so far back as the year 1803, when Desrone announced that he had extracted from it a peculiar crystalline substance, in which he believed its narcotic properties to reside. In a chemical point of view, his investigation was of minor importance, and it would scarcely merit notice, if it were not that it had an important influence in starting the idea which has proved so prolific in important results, that the therapeutic properties of medicinal substances depend upon the presence of particular active principles readily separable from the inert matters of which their bulk is composed. Desrone evaporated the aqueous solution of opium to a syrup, and, after allowing it to stand for some time, a gritty matter deposited, which was scarcely soluble in water, but crystallised easily from alcohol and ether. From his description of its properties it was obviously narcotine; but he did not observe its power of combining with acids, and his observations were far from definite, and did not attract much attention.

No one, indeed, appears to have followed them up until the year 1817, when Sertürner made the next step in the investigation of opium, and published the result of researches which had occupied him for several years. He detected meconic acid and morphia, but curiously enough failed to obtain Desrone's substance, which he therefore supposed to have been a meconate of morphia.

A considerable time again elapsed without any further progress being made; but in 1826 Dublanc discovered meconine, and described its properties very distinctly, although he did not give it a name—an omission supplied by Couerbe in 1830. During the several years following the latter date, opium was subjected to a very minute investigation by Couerbe, Pelletier, Robiquet, Merck, and others, who added codeine, thebaine, narceine, and porphyroxine to the list of its crystalline constituents. Subsequently to their time, little was done except to add a few analyses of the substances discovered by these observers, but without extending in any marked degree our knowledge of their chemical relations, until 1844, when Wöhler and Blyth separately examined narcotine, and made it the starting point of a very remarkable series of products.

In the year 1850 I was myself induced to commence the study of some of the principles of opium; and at that time I found our knowledge sufficiently extensive, but greatly deficient in precision. The constitution of meconic acid, morphia, and narcotine appeared sufficiently established; that of codeine was expressed by several different formulæ, of which, one recently proposed by Gerhardt had probability in its favour, and was fully confirmed by my own researches; but all that was known regarding the other subtances was in the last degree unsatisfactory, and based on the imperfect and often conflicting statements of their discoverers, and on analyses made at a time when the methods in use were deficient in that accuracy and precision which they have since attained. It was obvious indeed that the whole subject required revision, and I made it my task to do this in the first instance; but I was naturally led to extend my investigation to the study of the products of decomposition of the different substances, so far as the amount of material at my disposal permitted, and I am still engaged with the subject.

The mass of facts which has now been accumulated regarding the chemistry of opium renders it necessary for me to discuss it very succinctly here, and without entering into details. I pass altogether without mention its indeterminate constituents, although many curious observations have been made in relation to them, and proceed at once to the crystalline substances of which no fewer than twelve—nine well-determined and three doubtful—have been described. They are—

Morphine.
Codeine.
Papaverine.
Narcotine.
Thebaine.
Narceine.
Meconine.
Pseudomorphine?
Porphyroxine?
Opianine?
Meconic acid.
Thebolactic acid.

A critical review of the processes employed for the preparation of these substances would be of much interest, though by no means suited to the present occasion. It is very obvious that the results obtained by different experimenters have greatly depended on the methods they have pursued. We observe that one individual obtains particular substances abundantly, another only in very small quantity, and the difference is often due to modifications in the mode of working, which, at first sight, appear very trifling. Even the quantity of water employed in the primary solution of the opium is important, and greatly affects the quantity of resinoïd matters dissolved, and, by consequence, the facility with which some of the bases are made to separate in the crystalline form. Thus I have found narcotine very abundantly, while other observers obtain it in small quantity, and have altogether failed to detect pseudomorphine and porphyroxine, although I have sought for them with some care; nor have I noticed thebolactic acid, which the Messrs. Smith state they separate in large quantity. It is true that my attention has not been directed to the acids of opium; but had the substance in question been easily obtainable in the course of the process I have followed, it could scarcely have been overlooked. The investigator of opium is placed at a certain disadvantage by the necessity of making use of the refuse of the manufacture of morphine by processes in which everything is sacrificed to obtaining the maximum quantity of that alkaloid, irrespective of the others associated with it, and for the preparation of which it by no means follows that they are equally advantageous, and it can scarcely be doubted that, if it were possible to operate on a hundred weight or two of opium by methods entirely different from those now in use, results of much interest might be obtained.

For the preparation of morphine, the process originally proposed by Robertson and Gregory, has, in this country at least, proved itself the most suitable, and in skilful hands, is found to yield a larger proportion of the base than any other. It is so well known, that it is hardly necessary to refer to it here, the more especially as, so far as I know, no change has taken place in the principle on which it is founded, although, of course, there is abundant scope for judgment and skill in carrying out the manipulative details. The principle involved is very simple. The bases are present in opium chiefly as meconates, which are difficultly crystallisable salts; but on the addition of chloride of calcium, meconate of lime precipitates, and the chlorides remain in the solution, of which the hydrochlorates of morphine and codeine are readily crystallisable, and separate from the concentrated solution, leaving the other bases behind in the mother-liquor. It is from the residue left, after complete separation of the morphine, that I have extracted the bases I examined, and the process I have found most convenient is the following:—

The mother-liquor, which has the consistence of treacle, and is perfectly black, is diluted with water, and ammonia added. An abundant dark-brown precipitate falls, consisting of narcotine, papaverine, and thebaine, accompanied, as I have recently observed, by a small quantity of codeine, the presence of which could scarcely have been expected, and all contaminated with a brown resinous substance. This precipitate, which is at first quite granular, runs together into a resinous mass, if allowed to lie in the fluid, and the mother-liquor is thus squeezed out of it as effectually as if it were put into a powerful press. By solution of this precipitate in boiling spirit, impure crystals of narcotine are obtained on cooling, which may be purified by animal charcoal and successive crystallisations. By distilling down the solution, a further crop of crystals is dissolved, and finally a dark mother-liquor is obtained, from which *thebaine* and *papaverine* may be prepared. For this purpose water is added; the liquid is rendered slightly acid by acetic acid; and the resin which is thus separated is filtered off; subacetate of lead is then added to the filtrate until it restores the blue of reddened litmus; and the precipitate being separated, the excess of lead is removed by sulphuretted hydrogen, or more conveniently by sulphuric acid. Ammonia then precipitates the thebaine, still contaminated with resinous matters, from which it is separated by crystallisation from absolute alcohol, and decolorised by animal charcoal. Papaverine may be extracted from the lead-precipitate by digesting it with alcohol, evaporating the liquid, treating it with hydrochloric acid, filtering from resin, concentrating, and leaving the solution to itself for some time, when the sparingly soluble hydrochlorate of papaverine slowly crystallises. Precipitation with ammonia and crystallisation from spirit, give the base itself in a state of purity.

The mother-liquor from which the precipitate of these bases has been separated, contains *narceine* and *meconine*, with a small quantity of papaverine. On concentrating it, narceine separates in abundance, and is easily obtained pure by washing with a small quantity of cold water, and crystallisating two or three times. It is remarkably distinguished by the facility with which it is obtained free of colour, for which purpose animal charcoal is not required.

After concentrating the liquid, until the narceine is separated, the residue is agitated with ether, which extracts meconine, together with a little papaverine.

Meconic acid is prepared from the meconate of lime, obtained in the first part of Robertson and Gregory's process, according to a method well-known. Of the preparation of thebolactic acid, no description has yet been published.

Morphine, by far the most important of the constituents of opium, is as yet but imperfectly examined. Its constitution, long expressed in chemical works by the formula $C_{35}H_{20}NO_5$; this formula was altered by Gerhardt to $C_{34}H_{19}NO_6$, which has been universally adopted, and confirmed by subsequent researches. Little is known regarding the products of its decomposition; but the researches of How have shown that it belongs, like most of the other natural alkaloids, to the group of nitril bases. It exists in opium to the extent of about 10 or 12 per cent., but the proportion differs greatly in different varieties, being largest in opium produced from the poppy grown in this country, which is said to have yielded as much as 20 per cent., while in East India and in Egyptian opium it often does not exceed 5 or 6 per cent. Turkey opium is that from which it is most commonly extracted, but even then its quality varies very greatly; and as the amount contained in different specimens is a matter of much importance to the manufacturer, various attempts have been made to devise a method by which the amount contained in a given sample might be quickly and accurately ascertained. Mohr and other chemists have given processes for this purpose; but none of them have proved trustworthy, the fact being that the conditions under which morphine is completely separated, differ for every sample, and the manufacturer finds it much safer to rely upon his eye, which enables an experienced observer to form an opinion which, if not always correct, is safer than any chemical process.

The introduction of Robertson and Gregory's process led to the discovery of *codeine*, Robiquet having observed that when the morphine was precipitated from the muriate obtained by it, another base remained in solution along with the sal-ammoniac formed. His idea was that the liquid contained a double salt of codeine and ammonia. But I have satisfied myself that this view is erroneous, having obtained pure hydrochlorate of codeine from the liquid by crystallisation alone.

The earlier analyses of codeine led to the conclusion that it differed from morphine by a single equivalent of oxygen, and it was represented by the formula $C_{35}H_{20}NO_6$, which was called in question by Gerhardt. He made two analyses of the hydrated base, and obtained results corresponding with $C_{36}H_{21}NO_6$, which I have fully confirmed. Codeine, therefore, so far as its constitution is concerned, may be considered as a homologue of morphine, but they present none of that similarity in properties which is usually so conspicuous in the adjacent members of a homologous series. Nothing, indeed, can be more marked than the difference between morphine, insoluble in water and ether, and but sparingly dissolved by alcohol, and codeine, which is readily and abundantly taken up by all these menstrua. Other differences also exist, which render it very questionable whether the two bases can be considered as homologous. Codeine yields many beautiful substitution-products, which are obtained with some difficulty. I have described nitro-codeine $C_{36}H_{20}(NO_4)NO_6$, chlorocodeine $C_{36}H_{20}ClNO_6$, and bromocodeine $C_{36}H_{20}BrNO_6$, all obtained by the cautious action of the different substances on the base itself, and remarkably definite compounds. Indications of an iodine substitution-compound were also obtained; but the most remarkable iodine-compound is that which I have called teriodocodeine, without intending thereby to define its chemical nature. It contains the elements of one equivalent of codeine and three equivalents of iodine, and belongs to a class of compounds of whose rational constitution we have no definite ideas. It is obtained in beautiful doubly oblique crystals, displaying the phenomena of pleochroism in a very striking manner.

Thebaine was discovered by Pelletier in 1832, and described by him under the name of paramorphine, his analysis having led to the conclusion that it was isomeric with morphine; the inaccuracy of this opinion was shown by Couerbe and Kane, although neither of them succeeded in fixing its true constitution. My own analyses show that it contains $C_{38}H_{21}NO_6$, thus differing from codeine by two equivalents of carbon. It is quite insoluble in water, but extremely soluble in alcohol and ether, from the former of which it is deposited in tabular crystals on cooling. Strong sulphuric acid produces with it a deep red colour. When diluted, the acid dissolves it, and on standing for some time, a resinous substance deposits, which, on treatment with boiling water, dissolves, and on cooling, gives sparingly soluble crystals. Its salts crystallise well. Of its decomposition-products, nothing is yet known, but as I have now obtained a larger quantity of the base, I trust I may, at no distant date, be enabled to supply some information on this point.

Papavereine.—This base was discovered by G. Merck in 1850, and was obtained from an old opium residue. It appears, however, to be an invariable constituent of opium, and in not inconsiderable quantity. It is obtained in small needles, generally grouped in radiated masses, highly soluble in boiling alcohol and distinguished from the other opium-bases by giving a fine blue with concentrated sulphuric acid. Its salts crystallise well, the hydrochlorate more particularly being obtained in fine crystals. Its formula is $C_{40}H_{21}NO_8$. One of its most singular peculiarities is its tendency to carry down with it ammonia, when precipitated by that base; both Merck and myself obtained in its analysis a quantity of nitrogen considerably in excess of the theoretical quantity, and it was only by precipitating with potash, that I succeeded in obtaining an accurate result. It yields several well-marked substitution products, among which, nitropapaverine, which crystallises in pale buff needles, and yields sparingly soluble salts, and bromopapaverine, are the most characteristic.

Narceine is distinguished from all the other opium-bases by its solubility in water, whence it crystallises in fine silky needles, which are deposited in such abundance that a solution saturated at the boiling point becomes nearly solid on cooling. Its basic properties are very feeble, so much so indeed, that both Pelletier, its discoverer, and Couerbe who afterwards examined it, maintain, that it is incapable of combining with acids; but in this respect they were in error, for it gives well-marked salts. Its formula is $C_{46}H_{29}NO_{18}$. Its decompositions are as yet unknown, but I have observed that it is capable of producing certain substitution-products, and also of undergoing further changes, which I intend to investigate further.

Narcotine is by far the most interesting and remarkable of the opium-bases. Indeed, its remarkable decompositions, and the number of highly crystalline products it yields, give it claims to be considered as the most interesting of the natural alkaloids. Although discovered by Desrone at the beginning of the present century, its chemical history may be said to date from the year 1844, when Wöhler and Blyth separately obtained some of its most important decomposition-products. Wöhler found that, when treated with oxide of manganese and sulphuric acid, it yielded a new base and acid, which he called *cotarnine* and *opianic acid.* Blyth, in endeavouring to determine the constitution of narcotine by the analysis of its platinum-salt, observed that an excess of bichloride of platinum produced the same decomposition. His investigation led him to the conclusion that its formula was $C_{46}H_{25}NO_{14}$, which afforded a sufficient explanation of the results obtained by Wöhler and himself, and also harmonized with the researches I made at a subsequent period. More recently, Messrs. Matthiessen and Foster have again revised the formula of narcotine, and give $C_{44}H_{23}NO_{14}$ as the nearest expression of their results, and as likewise affording an easy explanation of its products of decomposition. It is not possible, in the present state of our knowledge, to decide positively between these two formulæ, and a similar uncertainty exists as to that of cotarnine, for which Blyth's analyses give $C_{26}H_{13}NO_6$, and those of Matthiessen and Foster $C_{24}H_{13}NO_6$; but there is no doubt as to the constitution of the non-nitrogenous substances produced along with it. Wöhler and Blyth obtained only opianic and hemipinic acids by treating narcotine; but by using nitric acid, I obtained, in addition, another substance which proved to be meconine, a base long before obtained by Couerbe, existing ready formed in opium, and having the formula $C_{20}H_{10}O_8$. Opianic and hemipinic acids, which are simultaneously produced, may be considered as higher degrees of oxidation of this substance, being respectively $C_{20}H_{10}O_{10}$ and $C_{20}H_{10}O_{12}$. The explanation of the decomposition of narcotine by oxidising agents must differ according as we accept the formulæ of Blyth, or those of Matthiessen and Foster. According to the former, narcotine may be represented as if it were a compound of meconine and cotarnine, plus hydrogen. Thus—

$$C_{46}H_{25}NO_{14} = C_{20}H_{10}O_8 + H_2 + C_{26}H_{13}NO_6,$$

and the action consists in the oxidation of two equivalents of hydrogen, while the further addition of two or four equivalents of oxygen would produce opianic or hemipinic acid. According to the latter view, narcotine would be simply a compound of meconine and cotarnine, thus—

$$C_{44}H_{23}NO_{14} = C_{20}H_{10}O_8 + C_{24}H_{13}NO_6,$$

and in that case the formation of opianic and hemipinic acids would be due to the direct addition of O_2 or O_4, while the breaking up into meconine and cotarnine must be explained upon a different principle. An experiment made by me long since, and to which reference is made at the close of one of my papers,* may serve to throw some light on this point. I exposed narcotine along with a slight excess of sulphuric acid, to a heat of 280° F., in a sealed tube, and thus obtained sulphate of cotarnine and meconine, and we may suppose that when the latter substance is obtained by the action of nitric acid, the change in both cases may be due to the strong acid simply expelling the meconine from its combination with cotarnine. It is fair to say, however, that the action is not so simple as here represented, and I invariably found that a dark-coloured substance was produced at the same time, the properties of which I have not yet examined.

Meconine or opianyl, as I prefer to call it, opianic and hemipinic acids, as well as cotarnine, are capable of yielding an extensive series of products of the most interesting kind, the relations of which are, however, far from being as yet completely worked out, and the discussion of whose properties would carry us far beyond the limits of the present paper. It is impossible, however, to avoid mentioning the facility with which they all yield methyl-compounds. Thus narcotine, when treated with hydriodic acid, gives 3 equivalents of iodide of methyl, and cotarnine and its products give methylamine with great ease. This is particularly the case with apophyllic acid, which, when boiled with excess of potash, evolves it readily, and an acid free from nitrogen is obtained. Apophyllic acid, which is formed by the action of nitric acid on cotarnine, is $C_{16}H_7NO_8$, and my observations lead me to suppose that it is a methylamic acid; should further investigations establish this, it would be represented by the formula $C_{14}H_2(C_2H_5N)O_8$, and contain an acid, $C_{14}H_4O_{10}$, which must bear a near relation to meconic acid, thus—

Supposed new acid	$C_{14}H_4O_{10}$
Meconic acid	$C_{12}H_4O_{10}$

Some years since Wertheim announced that he had ascertained the existence of three different kinds of narcotine in opium, which he called methylo-, ethylo-, and propylo-narcotine. These substances, however, I have been unable to detect, although a considerable number of different specimens of narcotine have passed through my hands; and as Messrs. Matthiessen and

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* Edinburgh Philosophical Transactions, vol. xxi., part i.

Foster have come to the same conclusion, little doubt can be entertained that Wertheim's idea is erroneous.

It will scarcely be necessary for me to refer at length to the three doubtful constituents of opium, except to say that they require further investigation. I must observe, however, that although I have followed, as nearly as circumstances would permit, the process given for their preparation, I have failed to detect the slightest indication of them; and it is probable that they are met with only in particular kinds of opium and in exceptional circumstances. This is certainly the case with opianine, which Hinterberger states he found in Egyptian opium, and in regard to which his statements are very imperfect. He originally gave for it the formula $C_{66}H_{36}NO_{23}$, which he afterwards altered to $C_{66}H_{36}N_2O_{21}$, but in neither case is there any satisfactory evidence of the accuracy of the results. Still less can be said for the formula $C_{27}H_{18}NO_{24}$ assigned to pseudomorphine, and as to porphyroxine nothing is known.

It has often been a matter of discussion whether these substances, which have been obtained from opium, are to be considered as educts or as products, that is, whether they pre-exist in it, or are the result of decompositions occurring during the process of extraction. As a chemical question, it would, of course, be most interesting to ascertain that they were products. The discovery of the decomposition of narcotine, with the production of meconine, may be taken as pretty conclusive evidence that it at least is a product; and if so, it may be fairly inferred that cotarnine must exist in the opium, although it has not been detected therein. Those, however, who are best acquainted with the properties of that base, will best understand the difficulty which besets its separation from such a substance a opium, and will not be inclined to doubt that it must exist there.

As regards all the other constituents of opium, they must be considered as educts, for notwithstanding a tolerably close connection between the *formulæ* of some of them, there is no evidence as to any relationship in constitution. We speak, however, on this point in ignorance; for what has now been said, is sufficient to show that, notwithstanding the mass of facts accumulated, our knowledge of many of the opium constituents is far from perfect, and that there is abundant scope for further investigation.

LIII.—*On the Constitution of Melampyrin.*

By Dr. ERLENMEYER and J. A. WANKLYN, Esq.

IN our paper on Mannite* we remarked that, notwithstanding the abundance of that substance, and the labour which had been bestowed upon its investigation, chemists were by no means sure of its formula. We showed further that, by subjecting that body to the action of hydriodic acid, iodide of hexyl was formed; and thus we established the formula which is in general use.

But if a degree of doubt existed as to the real composition of mannite, what shall we say about the composition of the rare members of the mannite family, some of which, obtained in small quantities from rare plants, have been investigated only by their discoverers.

In a recent paper, bearing the title "On the identity of Melampyrin with Dulcit,"† Gilmer has pointed out, very strikingly, one of the peculiar difficulties which beset the investigation of this class of compounds. Gilmer analysed melampyrin, and then found that there were three probable formulæ, which expressed his analysis:—

	$C_5H_{12}O_5$	$C_6H_{14}O_6$	$C_7H_{16}O_7$
C	39·47	39·56	39·62
H	7·90	7·70	7·55
O	52·63	52·74	52·83
	100·00	100·00	100·00

To distinguish between these three bodies, Gilmer prepared a crystalline baryta-derivative. Between $C_6H_{12}Ba_2O_6$ and either $C_5H_{10}Ba_2O_5$ or $C_7H_{14}Ba_2O_7$ there is a difference of from 1·5 to 2 in the percentage of carbon, so that an analysis is capable of determining the difference. Gilmer has fixed upon the formula $C_6H_{12}Ba_2O_6$, and consequently he writes $C_6H_{14}O_6$ for melampyrin.

We have been, for some time back, investigating the action of hydriodic acid upon different members of the sugar and mannite group. On the present occasion, we publish our experiments on melampyrin. As will be evident by-and-bye, we likewise fix upon the formula $C_6H_{14}O_6$, but we think it will be conceded that the method which we are adopting is calculated to furnish results of higher certainty than that followed by Gilmer. Here are three iodides corresponding to the three probable formulæ for melampyrin:—

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* Proceedings of the Royal Society of Edinburgh, 1861–62.

† Ann. Ch. Pharm. cxxiii, 372.

	$C_5H_{11}I$	$C_6H_{13}I$	$C_7H_{15}I$
C	30·30	33·96	37·17
H	5·56	6·13	6·64
I	64·14	59·91	56·19
	100·00	100·00	100·00

The carbon-difference is, as will be observed, between 3 and 4 per cent. Furthermore, there is a wide difference between the boiling points of these iodides; and from each one, derivatives may be got which present all manner of physical differences.

But there is another particular to which we would direct attention. Gilmer's baryta-derivative can, at the utmost, only establish that the molecular weight of melampyrin requires the formula $C_6H_{14}O_6$. It leaves quite unanswered the question, is the carbon group C_6 contained in the compound? Still, the question might be proposed, has melampyrin the nature of an ether? It leaves unnegatived these formulæ, for instance:—

$$C_6H_{14}O_6 = \left.\begin{array}{l}C_5H_8(HO)_3\\ C\ H\ (HO)_2\end{array}\right\}O \quad \ldots\ldots \quad (1)$$

$$C_6H_{14}O_6 = \left.\begin{array}{l}C_4H_6(HO)_3\\ C_2H_3(HO)_2\end{array}\right\}O \quad \ldots\ldots \quad (2)$$

$$C_6H_{14}O_6 = \left.\begin{array}{l}C_3H_4(HO)_3\\ C_3H_5(HO)_2\end{array}\right\}O \quad \ldots\ldots \quad (3)$$

By operating with hydriodic acid this question is at once set at rest. The obtaining of iodide of hexyl from melampyrin, not only settles the molecular weight of that substance, but also shows that the carbon-condensation is 6.

Among the rather numerous members of the mannite family we shall perhaps find some examples of the ether-formulæ just given.

The details of our experiments upon melampyrin are these. The melampyrin which we used was obtained from E. Merk, of Darmstadt, from whom we have ascertained the following particulars relative to its preparation. It was obtained from *Melampyrum nemorosum* and *M. vulgatum*.

Obviously, it was of importance to test whether it was free from mannite. For this purpose, we availed ourselves of the striking difference between the solubility of the two bodies in cold water. The solubility of mannite at 16° C. is 16 in 100 parts of water. The solubility of melampyrin, on the other hand, at the same temperature is, according to Gilmer,* 3·4 in 100 parts of water.

We made a determination of the solubility of our melampyrin in water, and also, under precisely similar circumstances, a determination of the solubility of mannite.

Inasmuch as we took care to keep the solution of melampyrin for several hours in contact with a large excess of finely powdered melampyrin, it is obvious that if our melampyrin had contained any considerable proportion of mannite, we should have got a number nearly approaching to the solubility of mannite. Nothing of the kind was observed, for these are our results:—

I. 100 parts of water at 16·5° C. dissolved 2·94 parts of melampyrin.

II. 100 parts of water at 16·5° C. dissolved 16·07 parts of mannite.

Our melampyrin was, therefore, free from mannite. It was analysed with the following results.

·3353 grm. of the substance burnt with chromate of lead and a little bichromate of potash gave ·2384 grm. of water and ·4835 grm. of carbonic acid.

	Calculated.		Found.
C_6	72 ..	39·56	39·33
H_{14}	14 ..	7·70	7·90
O_6	96 ..	52·74	
	182	100·00	

In one operation 4 grm. of melampyrin were heated in a stream of carbonic acid with 60 cub. cent. of strong hydriodic acid (boiling at 124° C). The dark-coloured oily distillate was distilled in contact with water, after having been freed from excess of iodine by means of sulphite of soda. The colourless oil which distilled weighed 2 grm.

On a larger scale the reaction did not seem to be so neat, for in a second operation 20 grms. of melampyrin gave only 5·5 cub. cent. of crude iodide. The amount of hydriodic acid (boiling at 126° C.) which was used in this experiment was 230 cub. cent.

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* Ann. Ch. Pharm., cxxiii, 377. In Gilmer's paper, there is a press-error, 34 instead of 3·4, with which latter number Gilmer's experiment agrees.

The crude iodide which distilled over was washed with sulphite of soda and then redistilled in contact with water, and in a stream of carbonic acid. After being dried with fused chloride of calcium, it could be distilled alone without much decomposition taking place. It was slightly coloured, and boiled at 165° to 175°C. (We have previously found that iodide of hexyl boils between these points.)

Analyses of our product gave these results:—

I. ·2317 grm. burnt with chromate of lead, copper-turnings being used, gave ·1320 grm. water and ·2936 grm. carbonic acid.

II. ·2338 grm. gave ·1360 grm. water and ·2982 grm. CO_2.

III. ·5790 grm. were sealed up with ethylate of sodium and heated in the water-bath for several hours. The iodide of sodium so formed was precipitated with nitrate of silver. The iodide of silver obtained weighed ·6285 grm.

	Calculated.		Found.		
			I.	II.	III.
C_6	72	33·96	34·56	34·78	
H_{13}	13	6·13	6·33	6·46	
I	127	59·91	..	..	58·66
	212	100·00			

Hence, it will be seen that the liquid was iodide of hexyl, the difference between the percentage of carbon required by iodide of hexyl and that required by iodide of heptyl being more than 3.

In order to confirm our result, we digested some of the liquid with alcoholic solution of potash for several hours; we then distilled in the water-bath, and added water to the distillate. An oil, lighter than water, and having the smell of hexylene, separated. This oil was dried with chloride of calcium, and then distilled. It boiled at 68° to 70° C. (the boiling point of hexylene); the retort was dry below 90°C. It was next saturated with bromine, with which it combined with great violence. The resulting bibromide was analysed.

I. ·2803 grm., burnt with chromate of lead and a little bichromate of potash, gave ·29·58 grm. CO_2; the water was lost.

	Calculated.		Found. I.
C_6	72 ..	29·51	28·78
H_{12}	12 ..	4·92	
Br_2	160 ..	65·57	
	244	100·00	

which leaves no doubt as to the nature of the compound. Moreover, the slight deficiency of carbon was due to a trace of bromine-substitution: for at the end of the treatment, of the olefine with bromine, the escape of a trace of hydrobromic acid was noticed.

To resume. Melampyrin, free from mannite, is resolved by hydriodic acid into iodide of hexyl, according to the equation:

$$C_6H_8(HO(_6+11HI = C_6H_{13}I + 6H_2O + I_{10}.$$

The carbon-condensation of melampyrin is therefore the same as that of mannite. Identity between the two bodies we do not contend for; on the contrary, there is a difference in the readiness with which the reaction of hydriodic acid may be accomplished. Mannite is attacked very readily, malampyrine with greater difficulty.

A way of explaining the difference by means of formulæ, is by writing the peroxide of hydrogen in different places in the two bodies thus:

$$C_6H_8\ (HO)_6;\ C_6(HO)_6H_8$$

We do not insist upon this mode of interpretation; it is only one possible method among many.

We hope, in the course of a short time, to be able to publish an account of the various members of the sugar and mannite group. The following substances, we hope, will be ready very soon.

1. Dulcite.
2. Phycite.
3. Erythromannite.
4. Inosite.
5. Sorbite.
6. Quercite.
7. Glycogen.

The foregoing paper was nearly finished, when we read that

M. V. de Luynes had applied our method to the investigation of erythromannite. This body is particularly interesting, inasmuch as it is believed to be a mannite having the formula $C_4H_{10}O_4$, which should yield iodide of tetryl on treatment with hydriodic acid.

From M. de Luynes' communication, which appeared in the *Comptes Rendus* (Oct. 13, 1862), it seems that he boiled erythromannite with hydriodic acid, when a heavy, oily liquid distilled. This liquid, separated from the water, was redistilled several times, and then purified from excess of iodine by means of an alkali, and dried, when it boiled at 120° C. and had the composition of iodide of tetryl. We cannot pass over this notice, without remarking that it seems to us to be strange that M. de Luynes' iodide would bear the treatment to which he subjected it. Iodide of hexyl obtained from mannite would be utterly destroyed by such management; for we find that, even when freed from iodine, the crude product decomposes at low temperatures, evolving volatile liquids. It must be first distilled with water in a stream of carbonic acid; it then becomes pure and colourless, and may be dried and distilled *alone*, without decomposition. We need hardly remind M. de Luynes, that if the decomposition of which we speak did actually take place, the agreement of his analysis with the composition of iodide of tetryl, or of any other iodide, must be regarded as accidental, and as establishing nothing at all.

It is a pity that M. de Luynes did not obtain any derivative from his iodide. If he had sufficient material at command to determine the boiling point of the iodide, he must have had enough to obtain tetrylene by the action of alcoholic solution of potash. When he resumes his investigation, we would recommend him to try to get tetrylene and make the bibromide from it.

As M. de Luynes announces his intention of trying to get the other terms of the series from his iodide of tetryl, we will anticipate a portion of our history of the hexyl-compounds, which we have promised to publish when our research is tolerably complete.

Hexyl-alcohol may be prepared by heating iodide of hexyl with oxide of silver and water. There is produced, at the same time, a considerable quantity of hexylene (boiling point 70° C.), and also of another liquid of very high boiling point, most probably a *parahexylene*.

The alcohol, after repeated rectifications, boils constantly at 136° C. It is, therefore, abnormal: for 151° C. is the boiling point of the normal alcohol.

Its specific gravity at 0° C. is ·8327; it has a fragrant smell, very unlike that of amyl-alcohol. It is insoluble in water.

Mixed with concentrated sulphuric acid at 0° C it yields parahexylene, and no trace of hexyl-sulphuric acid.

We would particularly draw attention to the fact that iodide of hexyl tends to split up into hexylene and hydriodic acid when any attempt is made to obtain compound ethers from it. With aqueous solution of caustic potash iodide of hexyl may be boiled without decomposition. With alcoholic potash or sodium-alcohol it gives hexylene. With acetate of lead, or with oxalate of silver, it gives a considerable quantity of hexylene: whether there is formed acetic or oxalic hexyl-ether, as a bye-product, we have not yet established, but we suspect it.

Heidelberg, October 21, 1862.

LIV.—*On the Separation of Tin from Antimony, and on the Analysis of Alloys containing Lead, Tin, Antimony, and Copper.*

By Charles Tookey, F.C.S.,

Of the Metallurgical Laboratory, Royal School of Mines.

The separation of tin from antimony, with a view to their direct quantitative estimation, has hitherto been regarded as an analytical process involving considerable difficulty, on account of the similarity which exists in the behaviour of the compounds of those metals with reagents.

The method proposed by Gay Lussac consists in precipitating the tin and antimony together by means of a strip of zinc; the weight of the precipitated metals having been ascertained, they are then redissolved in nitro-hydrochloric acid, and the antimony separated from the diluted solution by a strip of tin, the amount of this metal originally associated with the antimony, being estimated by difference. The more recent method, by Rose, provides for the direct estimation of each metal, the separation being effected by fusing the oxides with hydrate of soda, and digesting the antimonate and stannate of soda produced, with diluted alcohol, the insoluble antimonate of soda being afterwards washed on a filter with alcohol of increased strength as the operation of washing approaches completion.

Having had occasion to examine some alloys containing lead, tin, and antimony, with small quantities of copper, and having failed to obtain sufficiently accurate results in the separation of tin from antimony by either of the processes mentioned, I made several attempts to effect the object in view, but without success, when the reaction between the sulphides of tin and antimony and hydrochloric acid (gas) occurred to me as likely to afford a method free from objection.

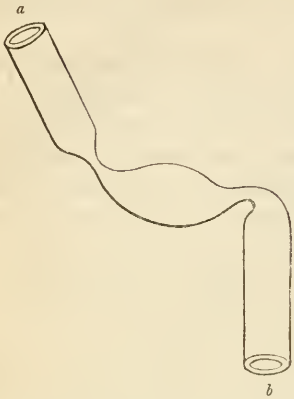
When tersulphide of antimony is exposed to the action of hydrochloric acid (gas), decomposition is effected at the ordinary temperature, with production of sulphide of hydrogen and terchloride of antimony, which, when gently heated, is easily volatilized in a current of the gas. Protosulphide of tin, when treated in a similar manner, is also decomposed, the products of decomposition being sulphide of hydrogen and proto-chloride of tin, which may be heated to incipient fusion in an atmosphere of hydrochloric acid, without undergoing any further change. A necessary condition, therefore, to the success of a separation by means of the reactions just stated, would be that the tin should exist in solution in the state of protoxide. By the method of analysis to be further described, the tin was obtained in the state of bichloride, and in endeavouring to effect the reduction of the bichloride to the state of protochloride, an experiment was made to ascertain the action of metallic iron upon the mixed chlorides of tin and antimony, in presence of an excess of hydrochloric acid, the result of which was, that while the bichloride of tin was reduced to protochloride, the whole of the antimony appeared to be separated in the metallic state.

Gmelin states, on the authority of Fischer, that iron does not precipitate tin from the protochloride at the boiling heat. To see how nearly separation could be effected by iron in the presence of hydrochloric acid, 6·03 grs. of pure antimony and 4·16 grs. of tin were dissolved in hydrochloric acid, with addition of a few drops of nitric acid; the solution was diluted with water, and, after adding more hydrochloric acid, digested at a gentle heat with 15 grs. of thin sheet iron, until the whole of the iron was dissolved; a considerable quantity of cold water was then added, and the antimony collected on a weighed filter, after being washed with water and dried, the antimony weighed 6·02 grs. In a second experiment, 9·145 grs. of pure antimony and 1·065 grs. of pure tin were dissolved as before; the antimony in this case after drying weighed 9·18 grs., the tin was precipitated from the filtrate by sulphuretted hydrogen, the protosulphide of tin dried, and converted into binoxide by careful ignition, the amount of binoxide obtained was 1·36 grs., containing 1·069 grs. of metallic tin.

In the analyses of the alloys containing lead, tin, and antimony, with small quantities of copper, the ordinary method for separating tin and antimony from other metals was used, viz., oxidation with nitric acid, the action being promoted by heat, and the excess of acid expelled by evaporation, the nitrates of lead and copper were removed by washing on a filter with hot water. By proceeding in this manner it was found, in two analyses of the same alloy, that the amounts of lead, and also the collective weights of the oxides of tin and antimony differed to a considerable extent. The same discrepancy was observed, whether the acid used for oxidation was in the concentrated state, or previously diluted with water. In order to ascertain the source of error, the oxides of tin and antimony were examined, and found to contain oxide of lead in a state of combination, in which it could not be separated by washing with water, and to see whether the application of heat affected the result, two equal weights (10 grs.) of the same alloy were taken, one was treated in the usual manner, heat being applied to promote the oxidation by nitric acid, the excess of acid being expelled by evaporation; boiling water was then added, and after perfect washing, the mixed oxides weighed, on ignition, 8·92 grs. The other was oxidized by nitric acid, without the application of heat, and the resulting oxides weighed 7·31 grs. The application of heat causes therefore a large proportion of the lead to remain with the oxides of tin and antimony. When an alloy of lead and antimony is heated with nitric acid, the latter metal is converted into antimonic acid, which combines with the oxide of lead, the resulting compound being insoluble in water.

That the whole of the lead might be separated from the other metals, the following process was employed. The alloy was oxidized by nitric acid, but little more acid being used than was necessary for oxidation; after removing the excess of acid by evaporation at a low temperature, the residue was digested with hot water, the oxides of tin and antimony being collected on a weighed filter, and after perfect washing, dried at 110—120° C. After ceasing to lose weight, they were carefully transferred to a glass boat; the filter with the small portion of oxides still adhering to it was again dried and weighed, the difference between the two weights giving the amount of oxides operated upon. The boat was then placed in a condensing apparatus, through which a slow current of hydrochloric acid was transmitted, and when the contents of the boat had become liquid from the absorption of gas, a gentle heat was applied in order to distil over the chlorides of tin and antimony. When the distillation was nearly finished, a greater heat was used to expel the last traces of bichloride of tin, and, the tube having cooled, the boat was withdrawn, and its contents (chloride of lead) dissolved out, and added to the solution containing the nitrates of lead and copper. These two metals were determined as usual, the solution being evaporated nearly to dryness, with a slight excess of sulphuric acid, the sulphate of lead washed with water acidified with sulphuric acid, and the oxide of copper precipitated from the filtrate by a solution of potash. The chlorides of tin and antimony were poured into a small beaker; the apparatus rinsed out with dilute hydrochloric acid, and, after adding more hydrochloric acid, the solution was heated gently and digested with metallic iron (as pure as possible) until the whole of the iron had dissolved, cold water was then added, the antimony collected on a weighed filter, and after washing with cold water, dried at 110° C. The filtrate from the antimony, if not sufficiently dilute, was mixed with water, and then saturated with sulphuretted hydrogen. The sulphide of tin being afterwards converted into binoxide by ignition.

In order to simplify the process as much as possible, the following plan was eventually adopted. Ten grains or more of the alloy to be analysed were introduced into a small piece of apparatus, having the following form, sufficient nitric acid to complete the oxididation was poured upon the alloy by means of a funnel-tube; the end *a* was corked, and the oxidation effected at a moderate temperature. When the alloy had been converted into a perfectly white mass, the excess of acid was expelled by attaching a tube and cork to *a*, and causing a gentle current of air to traverse the apparatus, either by means of an aspirator, or a pair of bellows; during this operation the apparatus should be heated sufficiently to cause the evaporation of the excess of nitric acid. The end *a* was now connected with an apparatus for generating dry hydrochloric acid (which should be made from fused chloride of sodium and sulphuric acid), while the end *b* was immersed in a small quantity of water contained in a beaker; the remaining part of the operation may be conducted as in the former process, care being taken not to distil the volatile chlorides too rapidly, and to avoid the fusion of the chloride of lead until all the bichloride of tin has been expelled.



The iron employed to precipitate the antimony should be in the form of thin sheet, about three times the weight of the antimony present, being usually sufficient for complete precipitation. It is necessary that the flask for generating the hydrochloric acid be provided with a funnel-tube, dipping just below the surface of the fluid, in order to prevent the too rapid absorption of the gas by the water which is used to condense the chlorides of tin and antimony.

LV.—*On the Composition of the Amorphous Deposit in Healthy Urine.*

By Professor HEINTZ, of Halle.

[Communicated in a letter to Dr. Bence Jones, F.C.S.]

IN your paper on "The Composition of the Amorphous Deposits in Healthy Urine," at page 213, vol. xv., of the Journal of the Chemical Society, you state that I consider the deposit as a mixture of different acid urates, modified in form by the presence of other substances in the urine. I have nowhere said this. You will find my opinion founded upon my experiments at page 238 of Müller's Archives for 1845. I there say: "It is therefore certain that the amorphous sediment always contains urate of ammonia, urate of soda, and urate of lime, and more rarely urate of potassa and urate of magnesia;" and at page 260: "As I have already shown that the fine amorphous sediment consists of a mixture of urate of soda, urate of lime, and urate of magnesia, and that it has not only the same properties, but the same composition as the sediment prepared artificially, the cause of the natural sediment being deposited as a fine amorphous powder becomes very evident. This cause is the simultaneous precipitation of these three salts, one of which, the lime-salt, as I have shown in a former part of the paper, is always precipitated in the form of a fine amorphous powder, whilst the ammonia-salt and the soda-salt, when they are redeposited at the same time, from a solution containing common salt, frequently fall as a fine powder; but they more constantly form larger or smaller microscopic rounded masses."

You will see from this that I regard the simultaneous precipitation of the different uric acid salts as the cause of the formation of the amorphous deposit, and I do not consider that it depends on the presence of other substances in the solution.

I must add, however, that the misunderstanding you have fallen into is partly my own fault, inasmuch as I have not sufficiently distinguished in my paper the two kinds of amorphous sediments which are met with in the urine.

In the introduction I have only separated the crystalline sediment from the amorphous; although farther on I have divided the latter into the fine granular deposit, easily soluble in warm water, and the larger rounded deposit, which is with difficulty dissolved in warm water. This last form I have often produced artificially when only the urates of soda and ammonia were present, whilst I obtained the finer granular form with certainty only when lime was present. I therefore stated that the presence of lime was necessary for the formation of the fine granular amorphous deposit of urates.

As oxalate has been so frequently found in the sediments of urine, subsequently to the date of my experiments, it might be thought that the lime which I obtained, came from this source; but, in opposition to this, I must say, first, that I sometimes filtered the fresh made urine before it gave the deposit of urates, and at other times that I redissolved the amorphous deposit, filtered it, and then took the sediment which fell on cooling for examination, and that then I always found lime present; and, secondly, that in forming artificially the fine amorphous deposit, the presence of lime was always necessary. But as you have found no lime in the sediments which you examined, it is evident that my conclusion, that lime is absolutely necessary for the formation of the fine amorphous deposit of urates, must be limited.

The sediments which you examined contained much potassa, and I found it only rarely, and then in very small quantity. I therefore made my experiments on the artificial production of the amorphous sediments with fluids free from potassa, and, under these circumstances, I found that it was essential that lime should be present. I must therefore restrict my conclusion thus, that for the formation of the fine amorphous powdery sediment, lime must be present if potassa is absent.

LVI.—*On a Volumetrical Process for the Analysis of Waters.*

By Edward Nicholson, F.C.S., Staff Assistant-Surgeon.

The want of a process by which surgeons and other scientific men interested in hygienic matters, could easily make an analysis of water, has long been felt; and attempts have several times been made to supply the deficiency.

Professor Clark, of Aberdeen, indicated the tincture of soap as a test for the presence of earthy salts in water; he adapted a burette, with a special graduation, to the determination of the hardness of water by the tincture of soap, and drew up a table for calculating the amount of the different earthy salts corresponding to the quantity of soap decomposed by the water.

The beautiful experiments of Professor Clark, after some examination and criticism by Professor Playfair, Mr. Campbell, and others, was adopted by MM. Boutron-Chalard and F. Boudet, as the basis of the so-called "Hydrotimétriè," for which a prize of 2,000 francs was awarded them by the Academy of Sciences. These chemists adapted the soap solution of Professor Clark to a more complete determination of the earthy bases, and as their very useful method has been used to some extent in France, and is employed in the Hygienic Laboratory of the Army Medical School at Fort Pitt, I will give a brief outline of the process they employ.

The solution of soap employed by MM. Boutron-Chalard and Boudet, is of such a strength, that 23 degrees of their burette (equal to 2·4 c.c.) form a permanent lather on agitation with 40 c.c. of a solution of chloride of calcium, containing 0·25 grm. per litre. One degree is deducted for the excess of soap-solution requisite to form the lather significative of the termination of the reaction. These 22 degrees correspond then to ·01 grm. of chloride of calcium, or to a quantity of any other soap-decomposing substance, varying according to the relation of its equivalent to that of chloride of calcium. The number of degrees of soap-solution decomposed by 40 c.c. of a water, when multiplied by certain factors, given in a table, gives the amount of chloride of calcium, or of any other salt, *ad libitum,* contained in the water.

The operations for the analysis of water by this method, comprise the following determinations:—

1. The hardness of 40 c.c. of water; this hardness is caused by carbonic acid gas, lime, magnesia, and whatever iron and alumina may be present.

2. The hardness of 40 c.c. of water from which the lime has been precipitated by oxalate of ammonia; this gives the hardness caused by magnesia and by carbonic acid gas.

3. The hardness of 40 c.c. of the water from which carbonate of lime and carbonic acid gas have been expelled by boiling; this *permanent* hardness, after a deduction of 3 degrees for carbonate

of lime still remaining in solution, is owing to salts of lime other than carbonate, and to salts of magnesia.

4. The hardness of 40 c.c. of the boiled water from which the *permanent* lime has been precipitated by oxalate of ammonia; this gives the magnesian hardness.

5. The sulphuric acid is estimated by adding to 40 c.c. of water, a measured quantity of solution of nitrate of baryta, of known hardness; the hardness of the mixture is determined, and the loss of hardness indicates the hardness of the sulphuric acid contained in the precipitated sulphate of baryta.

The distinguishing features in this improvement of Clark's process, are the estimation of the permanent lime and magnesia salts, and of the sulphuric acid.

This easy method of estimating the more important constituents of water render this process most valuable in the economical analysis of waters, as a means of determining the effect of a water on steam boilers and in domestic operations, and also as a method for calculating the exact amount of lime that must be added to water, to eliminate the carbonic acid and carbonate of lime. But, apart from its economical value, considering the process in the point of view of chemical analysis, it is liable to some objections, and appears susceptible of certain improvements.

Two of the determinations are made after the addition of oxalate of ammonia; and I find that this introduces a possibility of error, since the oxalate of ammonia, when added even in small excess, either gives a peculiar hardness of its own, or else deranges the production of a lather, so as to render the result uncertain. It is also impossible to express the exact constitution of the solid ingredients of the water, or give any precise idea of their composition. No account is taken of the alkaline salts, and thus the advantages of the method are not fully brought out.

Impressed with the delicacy of the reaction given by the solution of soap, with the minutest quantity of earthy base, or of carbonic acid gas (·00002 grm. of lime will cause a detectable hardness of 1-7th of a degree), I have endeavoured to adapt this delicate test to a more complete and reliable method of volumetrical analysis; and I believe I have succeeded in bringing the process of MM. Boutron and Boudet, by several modifications and additions, to an exactitude which leaves little to be desired. I have also simplified the calculations, so as to render them even easier than those necessary in ordinary gravimetrical analysis.

The burettes employed are divided into tenths of cubic centimetres or degrees, each 0·1 c.c. = 1°. These, with two pipettes of 10 c.c. and 50 c.c. respectively, a few basins and beakers, a few three-ounce stoppered bottles, and a graduated litre-measure, form all the apparatus required.

The following solutions are employed as test-fluids :—

1. *An Alcoholic Solution of Soap.*—The solution employed by MM. Boutron and Boudet is made with hard Marseilles soap, and in consequence it is solid at ordinary temperatures. This is a great inconvenience, from the necessity of heating the test-fluid; but, after experimenting on a considerable number of soaps, Dr. Parkes has found that the soft potash-soap of the London Pharmacopœia is the best; and this has accordingly been used by me. The solution is made by dissolving the soap, without heat, in a mixture of equal weights of alcohol and water.

The soap-solution is made of such a strength, that 20 degrees (2 c.c.) are exactly equivalent to 50 c.c. of a water containing 0·1 grm. per litre (or 7 grains per gallon) of carbonate of lime, and on adding to 50 c.c. of such a water 22 degrees, a permanent lather is produced by agitation. This requisite excess of 2 degrees per 50 c.c. is to be deducted from all determinations of hardness.

2. A solution of *nitrate of baryta,* containing 0·26 grm. per litre and equivalent in point of hardness to the aforesaid standard water containing 0·1 grm. per litre of carbonate of lime. 50 c.c. of this solution mark 20 degrees.

3. A stronger solution of *nitrate of baryta* is usually employed; it contains 1·300 grm. per litre; 50 c.c. of it mark 100 degrees.

4. A solution of *nitrate of silver* containing 8·500 grm. ($\frac{1}{20}$ of the equivalent of the salt) per litre.

5. A solution of *oxalate of ammonia,* containing 0·355 grms. ($\frac{1}{200}$ of the equivalent of the salt) per litre.

6. A solution of *permanganate of potash* containing 0·159 grm. $\frac{1}{1000}$ of the equivalent of the salt) per litre.

The above graduation of the solutions has been adopted, as the important advantage is thereby obtained, of being able to calculate the quantity of any substance per litre of water, by multiplying the number of degrees obtained by the atomic weights of the substance. Thus—

20 degrees × 50 (eq. of $CaO.CO_2$) = ·1000 grm. per litre, of carbonate of lime.
20 degrees × 28 (eq. of CaO) = ·0560 grm. per litre, of lime.
20 degrees × 35·5 (eq. of Cl) = ·0710 grm. per litre, of chlorine.

The quantities thus obtained, when multiplied by 70, show the number of grains per gallon of water.

The Analytical Process.

1. 50 c.c. of the water to be analysed are measured by the pipette into a stoppered bottle of about three-ounce capacity. The soap-solution is gradually dropped in from the burette, the bottle being strongly shaken at intervals, until a lather begins to form on the surface. The soap-solution is then added more cautiously, and enough has been added, when the water, on agitation, presents an iridescent, large-bubbled lather, breaking down very slowly, and, after a few minutes, leaving the surface perfectly covered with a beady film, reconvertible into a lather on again agitating. After a little practice, the exact point where the lather becomes permanent is attained by the addition of one small drop, about one-sixth degree, of soap-solution. The process thus indicates the presence of ·0005 grm. per litre of lime.

Two degrees are deducted for the excess necessary to produce a lather. The number of degrees found represents the hardness due to lime, magnesia, iron, and carbonic acid gas. The alkaline salts usually found in water, have no effect on the soap-solution.*

2. The amount of *lime* and *magnesia*, and, by difference, of free *carbonic acid gas*, is found by taking the hardness of the water after expulsion of the carbonic acid gas. To this effect 50 c.c. of the water are evaporated to dryness with one or two drops of sulphuric acid, and the residue is ignited to expel excess of acid; if the vapours be offensive, the residue may be neutralized by a few drops of ammonia, before ignition. The residue is dissolved in 50 c.c. of distilled water, and the hardness is ascertained. Oxide of iron will remain insoluble; its amount is to be deducted from the carbonic acid.

3. The *lime* is determined by the well-known application of permanganate of potash to the oxidation of oxalic acid.

To 50 c.c. of the water, add 50 c.c. (or, if the hardness exceeds 50 degrees, 100 c.c.) of the standard solution of oxalate of ammonia, let the mixture stand in a warm place for an hour, and filter. The filtrate and washings are heated in a basin to about 70° C., with a few drops of hydrochloric acid, and the standard solution of permanganate of potash is added from a burette. Subtract the number of cubic centimetres of permanganate required for oxidation of the excess of oxalic acid, from the number of cubic centimetres of oxalate of ammonia added to the water: the difference gives the number of degrees of lime.

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* If the hardness exceed 80 degrees, or if much magnesia be present, the earthy soap often assumes a curdy form, deranging the production of a lather; in this case only 25 c.c. should be taken for experiment, the 50 c.c. being made up with distilled water.

50 c.c. of the permanganate-solution ought exactly to oxidise 50 c.c. of the oxalate of ammonia-solution.

4. *Determination of the Alkalies.*—The amount of lime and magnesia once obtained by the processes described, the ordinary process of estimating the alkaline salts by evaporating a certain quantity of the water with sulphuric acid, and weighing the resulting sulphates, is much facilitated. The lime and magnesian hardness have merely to be multiplied by the equivalents of sulphate of lime and of sulphate of magnesia, and the numbers thus obtained to be deducted from the amount of mixed sulphates per litre of water. I have however devised the following method for the volumetrical determination of the alkaline salts:—

To 50 c.c. of the water, ignited with sulphuric acid, as before described (2),* add 20 c.c., or more, of the stronger solution of nitrate of baryta, taking care that the hardness of the quantity added (2 degrees per 1 c.c.) be much greater than that of the water, as previously ascertained. If no alkaline sulphates are present, the amount of sulphate of baryta precipitated will be exactly equivalent in hardness to the amount of earthy sulphates; and the hardness, when ascertained by the soap-solution, will be exactly that of the baryta-solution added. If, for example, 20 c.c. = 40 degrees of baryta-solution have been added to 50 c.c. of water containing 35 degrees of sulphate of lime and of magnesia (total 40 + 35), 35 degrees of sulphates of baryta will be precipitated and the hardness will be reduced to 40 degrees, exactly the hardness of the baryta added. But, on the other hand, if sulphate of soda be present in the water, in addition to the earthy sulphates, a greater quantity of sulphate of baryta will be precipitated, and the hardness will be reduced to less than 40 degrees. Should it be reduced to 36 degrees, that will show that 4 degrees of alkaline sulphate were present.†

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* It may be as well, at process No. 2, to evaporat 200 c.c. of water with sulphuric acid, dissolve the ignited residue in 200 c.c. of distilled water, and take 50 c.c. for analysis.

† If 20 c.c. of baryta solution have been added, the excess of soap-solution, to form

5. The *chlorine* is determined in 50 c.c. of the water by the solution of nitrate of silver. If the quantity be very small, it is best to evaporate 500 c.c. of water to a small bulk, and count cubic centimetres as degrees.

6. The *sulphuric acid* is determined by adding to 50 c.c. of the water, 10 c.c., or more if necessary, of the stronger baryta-solution, and ascertaining by the soap-solution the hardness of the mixture. The loss of hardness from the precipitation of sulphate of baryta, gives the number of degrees of sulphuric acid.

7. *Iron* is determined in the usual manner by the permanganate of potash solution. 500 c.c. of the water are evaporated to a small bulk with hydrochloric acid; the iron is reduced by sulphurous acid, and estimated by the permanganate of potash solution. Ten cubic centimetres are counted as one degree of Fe^2O^3.

If silica be present, it will remain on redissolving the ignited sulphates, and if 200 c.c. of the water have been evaporated with sulphuric acid, it may be estimated by weighing.

In process 2, the oxide of iron becomes insoluble, and increases the amount of carbonic acid gas, from which it must be deducted.

All the processes here described are of very easy execution. The method of estimating carbonic gas is unequalled in exactness and facility of execution by any method I know, and the process for estimating the total capacity of saturation of the alkalies is extremely exact and satisfactory. The estimation of sulphuric acid, devised by M.M. Boutron and Boudet, is likewise of great precision.

I append examples of the calculation of an analysis performed by this process, to show the advantage obtained by the method of graduation I propose, in establishing an empirical formula for the salts contained in waters.

I. *Analysis of the Water supplied by the Chatham Water Company to Fort Pitt.*

	Degrees.	
1. Hardness	53°·7	Carbonic acid gas* Calcium .... Magnesium .... Iron ....
2. Hardness after ignition with sulphuric acid ..	49°·7	Calcium .... Magnesium ....
3. Calcium ascertained by permanganate	48°·3	Calcium ....

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a lather, will be greater; 2·8 degrees must be deducted. But it is perhaps better always to add 50 c.c. (100 degrees) of baryta. The deduction is then 4 degrees, and the loss of hardness on 100 degrees is the amount of alkali.

* The iron is to be deducted from the gross carbonic acid, 4 degrees.

	Degrees.	
4. Hardness after ignition with sulphuric acid, solution, and 60 degrees of baryta added	53°·6	(Sodium loss 6°·4)
5. Chlorine	5°·5	....
6. No sulphuric acid		....
7. Iron	0°·2	....

Deduction of an Empirical Formula for the Salts contained in the above Water.

This calculation, so tedious by the ordinary method, becomes here of extreme simplicity. I combine the 5·5 degrees of chlorine with an equal number of degrees of sodium, a balance of ·9 degrees of sodium is left. This with the calcium and magnesium is calculated as carbonate.

	Deg.		Equivs.		Grm.	per litre.		Grs. per gal.
Carbonate of lime ..	48·3	×	50	=	·2415	× 70	=	16·905
Carbonate of magnesia	1·4	×	42	=	·0058	× 70	=	·406
Carbonate of soda....	·9	×	53	=	·0047	× 70	=	·329
Chloride of sodium ..	5·5	×	58·5	=	·0321	× 70	=	2·247
Oxide of iron........	·2	×	80	=	·0016	× 70	=	·112
Silica				=	·0020	× 70	=	·140
					·2877			20·139
Carbonic acid gas	3·8	×	44	=	·0167 =		=	2·52 c.
	($2CO^2$)				8·93c.c.			in per gal.
Residue on ignition...............					·2810		=	19·68.

II. *Water from a pump at Fort Pitt.*

	Degrees.
Total hardness	36·8
Calcium and magnesium	21.0
Calcium	16·9
Sodium	5·0
Iron (Fe^2O^3)	1·2
Sulphuric acid	4·8
Chlorine	3·6

	Degrees.				Grm. per litre.			Grains per gal.
Carbonate of lime	16·9	×	50	=	·0845	× 70	=	5·915
Carbonate of magnesia	·7	×	42	=	·0029	× 70	=	·203
Carbonate of iron	1·2	×	116 2(FeO,CO^2)	=	·0139	× 70	=	·973
Sulphate of magnesia..........	3·4	×	60	=	·0204	× 70	=	1·428
Sulphate of soda..............	1·4	×	71	=	·0099	× 70	=	·693
Chloride of sodium............	3·6	×	58·5	=	·0210	× 70	=	1·470
					·1526			10·682.
Carbonic acid gas	14·6	×	44	=	·0642			=31·3c.c.pr.lit.
				(×	·537)			(31.3 c.c. × 4·54 × ·061)
								=8·67c. in. per gallon.

Solids by evaporation ·1500 per litre.

I may mention that the solution of permanganate of potash, of the standard here employed, answers admirably for the estimation of organic matter in water. 500 c.c. of water are heated to 70°C., with a few drops of pure sulphuric acid, and the standard solution is added, 1 c.c. at a time, until a colour, lasting for 10 minutes, is obtained. Every 10 c.c. of test-solution thus decolorised is equal to one degree of organic matter requiring one equivalent of oxygen for complete oxidation (corresponding to C^2O^3,HO, for example).

I may say a few words as to the best manner of attaining the rapidity which forms one merit of this process. I first set 200 c.c. of water to evaporate with a few drops of sulphuric acid for processes 2 and 4; I also precipitate the lime in 50 c.c. for process 3. By the time I have taken the total hardness, and estimated the chlorine, sulphuric acid and iron, the evaporation is finished and the residue ready to be taken in hand. Two or three analyses can thus be easily performed in a day. One point must be carefully observed: that the distilled water contain no carbonic acid gas. The delicacy of the soap-test for this gas is so great that the distilled water will speedily acquire one or two degrees of hardness, if left exposed to the air. If it has acquired any hardness from this cause, it should be boiled previously to use.

In conclusion I must beg to acknowledge my obligations to Dr. Parkes, who, by his discovery of the fact, that, contrary to expectation, potash-soap might be employed to make a soap solution perfectly fluid at ordinary temperatures, removed what would have been an insuperable bar to any perfection of the method of analysis.

LVII.—*On Hypobromous Acid.*

By William Dancer,

Dalton Scholar in the Laboratory of Owens College, Manchester.

Balard[*] in his original memoir on bromine, published in 1826, mentions that when bromine water is brought into contact with the alkalies and alkaline earths, dissolved or suspended in water, the smell and colour of the bromine disappear, whilst no oxygen gas is evolved, and that, on the addition of a weak acid to the solution, bromine is liberated; a reaction, observes Balard, which proves that bromine forms with these oxides a compound analogous to the so-called chlorides of lime and soda.

Many other chemists, especially Löwig,[†] Fritsche,[‡] and Gay Lussac,[§] mention the mode of preparing a bleaching salt of bromine with the alkalies, indicating the existence of hypobromous acid; indeed Gay Lussac states that this oxide can be obtained in the gaseous state by the action of bromine on dry oxide of mercury, but Pelouze showed that the gas thus produced was oxygen. Our knowledge concerning the properties of this oxide of bromine is, however, very limited, so much so that Berzelius states that even its existence is uncertain.

At the suggestion of Professor Roscoe, I undertook the investigation of this subject, and I have succeeded in establishing the composition of hypobromous acid in aqueous solution, and in determining some of its properties.

I have, however, been unable to prepare the hypobromous anhydride, as this body is far more unstable than the corresponding chlorine compound, and when liberated in the gaseous form, splits up, even at the ordinary atmospheric temperature, into bromine and oxygen.

In order to assure myself of the absence of chlorine in the bromine employed, the whole quantity of bromine was dried and distilled; the first portion of the distillate was collected separately, and a weighed quantity of this liquid reduced by aqueous sulphurous acid, and precipitated as bromide of silver; thus 2·3345 grms. of bromine yielded 5·486 grms. of bromide of silver, the theoretical weight of silver-salt obtainable from the above quantity of bromine being 5·487 grms. A second analysis was made by passing dry chlorine gas over a weighed portion of bromide of silver obtained from a similar quantity of bromine; 2·294 grms. of bromide of silver yielded 1·755 grm. of chloride of silver, a quantity closely corresponding to the theoretical amount of 1·751 grm. Hence we may conclude that the bromine employed was free from chlorine.

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[*] Ann. Ch. Phys., xxxii. 337.

[†] Pogg. Ann. xiv. 14, 485.

[‡] J. pr. Chem., xxiv. 291.

[§] Compt. rend., xiv. 951.

I.—*Action of Bromine on Aqueous Solutions of the Salts of the Alkalies and Alkaline Earths.*

(1). On shaking a strong solution of hydrate of potash or soda with bromine, no bleaching compound is formed, bromide and bromate of potassium only being produced.

(2). With a weak solution of hydrate of potash or soda, a slightly yellow liquid is obtained, which bleaches strongly; this must contain a compound of the alkali with hypobromous acid, as upon distillation, either under the ordinary atmospheric pressure, or *in vacuo,* the distillate does not possess bleaching properties, and becomes slightly coloured with free bromine.

(3). On shaking bromine-water with solution of the carbonate of potassium or sodium, carbonic acid is given off, and the liquid, which is of a light yellow tint, bleaches vegetable colours. On being heated to 30°C., or left for some time at the ordinary atmospheric temperature, bromine is liberated, and the solution becomes colourless, losing its bleaching properties.

(4). When an aqueous solution of phosphate of sodium is shaken up with bromine-water, a bleaching solution is produced; this, however, cannot be distilled even *in vacuo* without decomposition, free bromine being evolved.

(5). Bromine shaken up with solution of chloride of sodium does not yield a solution containing hypobromous acid, behaving with this salt unlike chlorine, which, according to Williamson, yields a solution from which free hypochlorous acid can be obtained by distillation.

(6). Solid hydrate of lime shaken up with bromine, absorbs it with evolution of heat, becoming coloured red. If a small quantity of water be added, the mixture gradually loses its colour, and gains the peculiar sweetish smell of bleaching powder; filtered from the excess of lime, the solution has a light yellow colour, and bleaches vegetable colours rapidly.

This solution, even when very weak, is decomposed by dilute nitric, sulphuric, and hydrochloric acids, behaving with these acids unlike the corresponding chlorine compound. Carbonic anhydride in excess, when passed into strong solutions, decomposes this salt, liberating bromine; but when this gas is passed slowly into a dilute solution, the hypobromous acid is not entirely decomposed, for on distilling *in vacuo* the distillate was found to contain hypobromous acid, as well as free bromine.

(7). Bromine water added to baryta-water partially loses its colour, and the solution possesses strong bleaching properties. A current of carbonic anhydride passed through the solution liberates bromine, and after some time precipitates the barium as carbonate. Hence it is evident that bromine forms with baryta compounds similar to those which it forms with lime.

II.—*Action of Bromine-water on Solution of Nitrate of Silver.*

When pure bromine-water is shaken up with excess of nitrate of silver solution, a liquid is produced which bleaches strongly (Spiller *). This liquid, on boiling, yields a distillate, of which the first portions contain much free bromine, but the later portions possess a light straw-colour, and still bleach vegetable colouring matters powerfully. If the distillation of the solution be conducted *in vacuo* under a total pressure of 50 mm. of mercury, the liquid boils at 40°C.; and all the distillates have a straw colour; they do not contain free bromine, they possess an acid reaction, and bleach strongly. If, however, the temperature rises to 60°C., the dark-coloured vapour of bromine appears in the retort, showing that at that temperature decomposition of the hypobromous acid ensues.

For the purpose of determining the composition of the bleaching substance here present, definite volumes (50 cbc.) of the almost colourless acid distillate were completely reduced with freshly prepared solution of sulphurous acid, and the excess of sulphurous acid was removed by rapid boiling. In one of the portions, the sulphuric acid formed was estimated as barium-salt; in the other the barium weighed as bromide of silver.†

For every 233 parts by weight of sulphate of barium obtained, the liquid contained 8 parts by weight of oxygen; out of every 188 parts of bromide of silver found, 80 parts of bromine were combined with this oxygen. Hence the relation between the quantities of bromine and oxygen in the compound is obtained.

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* Chem. News, 1, 38.

† According to the method proposed by Calvert and Davies for the analysis of hypochloric acid.—Chem. Soc. Journ., vol. ii., p. 193.

The following numbers give the experimental results, and show that bromine and oxygen are contained in the liquid in quantities represented respectively by the numbers 80 and 8 :—

I.—50	cbc. of distillate	yields	0·402	grms.	BaSO$_4$ and	0·324	grms. AgBr.
II.—50	”	”	0·222	”	”	0·183	”
III.—50	”	”	0·417	”	”	0·321	”
IV—60	”	”	0·389	”	”	0·323	”

Hence—

Calculated.		Found.			
		I.	II.	III.	IV.
Br 80·0	90·91	90·90	91·07	90·53	91·13
O 8·0	9·09	9·10	8·93	9·47	8·87
88·0	100·00	100·00	100·00	100·00	100·00

In order to determine whether half the total bromine in contact with nitrate of silver solution, is converted into hypobromous acid, two equal volumes of the same bromine water were taken, and in one portion the total bromine was determined after complete reduction with sulphurous acid, whilst to the other portion nitrate of silver was at once added, and the precipitated bromide of silver was weighed.

1. 50 cbc. Bromine-water reduced with sulphurous acid, yielded 1·206 grms. BrAg, or 0·513 Br.

50 cbc. Bromine-water not reduced with sulphurous acid, yielded 0·647 grms. BrAg, or 0·275 Br.

Hence 46·40 per cent. of the total bromine was contained in the form of hypobromous acid, and was not precipitable by nitrate of silver.

2. 50 cbc. Bromine-water reduced with sulphurous acid yielded 1·618 BrAg, or 0·6885 Br.

50 cbc. Bromine-water not reduced with sulphurous acid yielded 0·957 BrAg, or 0·4072 Br.

Hence 40·88 per cent. of the total bromine was contained in solution as hypobromous acid.

3. 50 cbc. Bromine-water reduced with sulphurous acid yielded 1·205 BrAg, or 0·5126 Br.

50 cbc. Bromine-water not reduced with sulphurous acid yielded 0·642 BrAg, or 0·273 Br.

Hence 46·74 per cent. of the total bromine was contained in solution as hypobromous acid.

On standing in contact with excess of nitrate of silver solution, aqueous hypobromous acid is slowly decomposed, and bromide of silver is precipitated; this explains the excess of bromide of silver found in the unreduced portions. From the above analyses it is however clear, that the decomposition in question really occurs.

On distillation at temperatures above 60°C., aqueous hypobromous acid is decomposed, free bromine being liberated and bromic acid formed. This is shown by the appearance in the retort of a difficultly soluble silver-salt, which crystallised in long needles, and was shown by analysis to be bromate of silver

III.—*Action of Bromine-water on Oxide of Mercury.*

Hypobromous acid is likewise formed when bromine-water is shaken up with finely divided protoxide of mercury, prepared either by igniting the nitrate, or by precipitation with potash.

After agitation for a short time with an excess of oxide of mercury, the whole of the bromine disappears; no oxygen gas is evolved, but the liquid assumes a light straw colour, possesses the peculiar sweetish smell characteristic of hypobromous acid, and bleaches strongly. This liquid when distilled under the ordinary atmospheric pressure, undergoes rapid decomposition; free bromine is given off in large quantities, and bromate of mercury remains behind in the retort. Under a pressure of 40mm. of mercury, when the liquid boils at about 30°C., the aqueous hypobromous acid distils over undecomposed.

By saturating aqueous hypobromous acid, thus prepared, with bromine, shaking again with oxide of mercury, and repeating these operations several times, a more concentrated aqueous solution of hypobromous acid can be obtained; 100 cbc. of a liquid which had been thus treated six times, was found to contain 6·21 grms. of combined bromine in solution. It is not possible, however, to obtain a pure distillate from a liquid prepared in this way, as the concentrated solution is decomposed even at 30° C., bromine being liberated in large quantities.

That the hypobromous acid, like the corresponding chlorine compound, is not combined with the oxide of mercury, is proved by the fact of its volatility. Owing, however, to the ease with which this body splits up into bromine and bromic acid, the hypobromous acid obtainable in the distillate is not equivalent to half the total quantity of bromine employed. In one experiment, 1,000 cbc. of bromine-water containing 10·44 grms. bromine, yielded on distillation only 2·818 grms. of bromine combined as hypobromous acid. In this respect, then, the lowest oxide of bromine differs from aqueous hypochlorous acid, which, as Gay Lussac showed, may be distilled when dilute, without any decomposition occurring.

The first portions of the distillate contain, however, by far the largest proportion of the acid, as is shown by the following determinations:—

1. 1,000 cbc. of bromine-water, containing 16·88 grms. of bromine, were shaken up with oxide of mercury, and the clear liquid distilled in vacuo at 30°C., under a pressure of 40 mm. mercury. Successive volumes of the distillate, amounting to 100 cbc. each, were analysed with standard silver-solution after complete reduction with sulphurous acid.

The 1st	100	cbc.	contained	0·736	grms.	bromine.
2nd	,,	,,	,,	0·560	,,	,,
3rd	,,	,,	,,	0·404	,,	,,
4th	,,	,,	,,	0·304	,,	,,
5th	,,	,,	,,	0·244	,,	,,
6th	,,	,,	,,	0·174	,,	,,
7th	,,	,,	,,	0·156	,,	,,
8th	,,	,,	,,	0·080	,,	,,

2. 1,000 cbc. of bromine-water, containing 10·00 grms. bromine, treated with oxide of mercury and distilled, gave the following results:—

The 1st	100	cbc.	contained	0·416	grms.	bromine.
2nd	,,	,,	,,	0·404	,,	,,
3rd	,,	,,	,,	0·240	,,	,,
4th	,,	,,	,,	0·124	,,	,,
Mean of the 5th, 6th, 7th	,,	,,	,,	0·113	,,	,,
8th	,,	,,	,,	0·024	,,	,,

In order to determine the proportion of the total quantity of bromine which, in contact with oxide of mercury and water, formed hypobromous acid, a solution of bromine-water, containing in 25 cbc. 0·2537 grms. of bromine, was shaken up with an excess of oxide of mercury until all the free bromine had disappeared; the solution was then filtered, and the mercury in the filtrate estimated as sulphide; 0·211 grms. of sulphide of mercury corresponding to 0·1455 grms. bromine, was obtained. In like manner, the filtrate from 100 cbc. of a second portion of bromine-water, containing 1·797 grms. of bromine, yielded 1·6365 grms. of sulphide of mercury, corresponding to 1·128 grms. of bromine. Hence it appears that in the one case 42·64 per cent. of the total bromine was converted into hypobromous acid, and in the other case 37·22 per cent. It is probable that a soluble salt of mercury and hypobromous acid is thus formed; this supposition would, at least, account for the excess of mercury found in the filtrate.

The extremely unstable character of the aqueous hypobromous acid, at the ordinary atmospheric temperature, is well shown by its behaviour with oxide of silver. When bromine water is agitated with finely divided oxide of silver in excess, hypobromous acid is immediately produced, and if the solution be quickly poured off from the excess of oxide and from the precipitated bromide which is formed, it possesses strongly bleaching properties; but if it be allowed to remain, even for a few minutes, in contact with the excess of oxide of silver, bubbles of oxygen gas are given off, bromide of silver is formed, the solution becomes colourless, and altogether loses its bleaching power. It is probable that hypobromite of silver exists in this solution; for if the solution, poured off quickly from the excess of oxide of silver, be allowed to stand for some time, it is found to decompose, bromide of silver being precipitated.

IV.—*Action of Bromine upon dry Oxide of Mercury.*

On acting with bromine upon an excess of dry oxide of mercury, prepared by igniting the nitrate, great heat is evolved; and, if the mixture be heated in a sealed tube at 100° C., a dry powder is formed which possesses the peculiar smell of bleaching-powder, and, when treated with water, gives a strongly bleaching solution. No bleaching substance is, however, formed when an excess of bromine is employed, a hard mass remaining in the tube, but in both cases large quantities of oxygen gas are liberated, causing the tubes to burst with a loud noise when the ends are opened with a file. The mercury, bromine, and oxygen contained in a portion of the powder from one of these tubes, were determined directly.

(a). *Determination of Bromine.*—1·1295 grms. of the mass left in the tube, was dissolved in nitric acid, and the bromine precipitated with nitrate of silver, 0·7195 grms. bromide of silver was obtained, corresponding to 27·11 per cent. bromine.

(b). *Determination of Mercury.*—1·1335 grms. of the same mixture was dissolved in hydrochloric acid, and the mercury precipitated by sulphuretted hydrogen, 0·8975 grms. HgS was obtained, corresponding to 68·28 per cent. mercury.

(c). *Determination of Oxygen.*—0·9575 grms. of the mixture was placed in a combustion-tube, closed at one end, containing some dry carbonate of manganese; after the air had been expelled from the tube by heating the carbonate, the mercury-salt was heated and the oxygen-gas collected over mercury; the apparatus was again swept out by the carbonic acid, and after this gas had been removed from the receiver by solution of caustic alkali, the oxygen was transferred to a calibrated eudiometer for measurement, care being taken to ensure the complete removal of the carbonic acid, by means of a potash ball. The volume of oxygen thus obtained reduced to 0°C. and 760 mm. Bar., amounted to 256 cbc., corresponding to 3·84 grms. in 100 grms. of the mixture.

From these data, the relative quantities of bromide of mercury, oxide of mercury, and hypobromite of mercury present in the mixture, can be calculated by the help of the three following equations:—

Let x equal the per centage weight of $HgBr$ in salt.
y ,, ,, ,, HgO ,,
z ,, ,, ,, $HgOBrO$,,

$$(1).\ \tfrac{100}{180}x + \tfrac{100}{108}y + \tfrac{100}{196}z = 68{\cdot}28$$

$$(2).\ \tfrac{80}{180}x + \tfrac{80}{196}z = 27{\cdot}11$$

$$(3).\ \tfrac{8}{108}y + \tfrac{16}{196}z = 3{\cdot}84$$

Or $x = 48{\cdot}62$ per cent. bromide of mercury.
$y = 37{\cdot}06$,, oxide ,,
$z = 13{\cdot}48$,, hypobromite ,,

99·16

Another portion of the bleaching salt was prepared, and analysed as before. The following results were obtained:—

(1). 0·869 grms. gave 0·3735 grms. $BrAg$ = 18.29 per cent. bromine.

(2). 0·871 grms. gave 0·7545 grms. HgS = 74·64 per cent. mercury.

(3). 1·688 grms. gave 588·3 cbc. O at 0°C. and 76 mm. = 5·00 per cent. oxygen.

Hence by substituting these numbers in the foregoing equations we have—

x = 31·50 per cent. bromide of mercury.
y = 55·89 ,, oxide ,,
z = 10·54 ,, hypobromite ,,

97·93

A portion of the contents of the tubes consisting of a hard solid mass was separated from the adhering powder, and analysed. This, as is seen by the following numbers, consists of a mixture of bromide and oxide of mercury, the former existing as a white crust surrounding the latter, the hypobromite in this portion having been probably decomposed either by the heat which was evolved during combination, or by an excess of bromine.

(1). 1·8355 grms. of the salt gave 1·032 grms. BrAg, corresponding to 23·92 per cent. of bromine.

(2). 1·644 grms. of salt gave 1·389 grms. HgS, corresponding to 72·85 per cent. of mercury.

(3). 1·782 grms. gave 399·5 cbc. of oxygen, at 0°C. and 76 mm., corresponding to 3·22 per cent. of oxygen.

Hence it is seen that the solid substance consisted simply of a mixture of bromide and oxide of mercury in the following proportions:—

Bromide of mercury = 56·25 per cent.
Oxide ,, ,, = 46·36 ,,

102·61

V.—*Attempts to Prepare Hypobromous Anhydride.*

All the methods used for obtaining hypochlorous anhydride fail when applied to produce the corresponding bromine compound. When dry chlorine is passed slowly over dry oxide of mercury, gaseous hypochlorous anhydride is formed. When, however, the same reaction is repeated with bromine, no hypobromous anhydride is formed, oxygen gas alone being produced, both at the ordinary atmospheric temperature, at 100°C., and at minus 18° C.

When bromine acts upon moist oxide of mercury, no oxygen gas is evolved, but the hypobromous acid is all absorbed by the water, and if the mixture be heated to a temperature above 30°C., it is decomposed, bromic acid and free bromine being the products.

The method used by Balard for preparing hypochlorous anhydride, by placing a saturated aqueous solution of the acid in a tube over mercury, and absorbing the water with nitrate of lime or phosphoric acid, does not give satisfactory results with hypobromous acid, for the strong aqueous acid is decomposed in contact with the mercury, and the gas which collects proves to be oxygen. The spontaneous decomposition of gaseous hypobromous anhydride, at the ordinary atmospheric temperature, into bromine and oxygen, was shown in the following manner:—About two ounces of oxide of mercury, together with six ounces of water, were put into a flask, half an ounce of bromine was added, and the whole well shaken up; as soon as the solution had lost its red colour, another portion of bromine was added, and it was again well shaken. This process was repeated (more oxide of mercury being occasionally added), until about five ounces of bromine had been used; the liquid, which did not smell of free bromine, was then filtered, and a small flask was completely filled with it, and this flask was connected by means of a piece of caoutchouc tubing (containing a Bunsen-valve), with a large bulb blown upon a thick piece of glass tube; the connections being made good, the bulb was attached to the air pump, exhausted, and the tube sealed off between the bulb and the air pump. When the valve between the exhausted bulb, and the flask was opened, gas possessing the colour of bromine was given off from the liquid, even at the ordinary temperature. After a short time the bulb was opened under water, no apparent absorption took place. Another bulb filled in a similar way, was opened under mercury, in a few minutes the gas became colourless, and the mercury rose in the tube. An eudiometric analysis was made of the residual gas, and the following results were obtained:—

No. 1. Analysis of gas evolved at the ordinary atmospheric temperature, and under reduced pressure.

	Vol.	P.	Temp.	Vol. at 0° and 76 mm.
Volume of gas employed..........	206·5	332·5	18·5	80·63
Ditto after addition of hydrogen ..	311·9	438·5	14·8	165·9
Ditto after explosion	246·2	362·0	12·6	107·3

The oxygen which remains, after deducting the calculated quantity required to form air with the nitrogen present, amounts to 3·26 per cent.

No. 2. Analysis of gas evolved at 25°C., and under reduced pressure.

	Vol.	P.	Temp.	Vol. at 0°C and 760 mm.
Volume of gas employed..........	191·87	324·7	9·0	77·34
Ditto after addition of hydrogen ..	389·06	514·2	9·5	250·10
Ditto after explosion	340·78	460·5	7·3	197·7

The surplus oxygen in this case amounts to 1·7 per cent. From this it is seen that the gas consisted of a mixture of air, oxygen and bromine, the two latter resulting from the decomposition of the hypobromous anhydride.

VI.—*Solubility of Bromine in Water.*

To the above experiments I have to add the following determinations of the solubility of bromine in water between 5° and 30°C. The numbers in the first column of the following table give the temperatures at which the solubility was determined; the numbers in the second column give the weight of bromine in grammes contained in 100 grms. of bromine-water at the corresponding temperature as the mean of several estimations:—

No.	I.	II.
1	5°C	3·600 grms.
2	10°	3·327 ,,
3	15°	3·226 ,,
4	20°	3·208 ,,
5	25°	3·167 ,,
6	30°	3·126 ,,

By help of graphical interpolation, the following numbers were obtained for the solubility of bromine in water between 5° and 30°C :—

Temp.	Bromine in 100 Bromine-water.	Temp.	Bromine in 100 Bromine-water.	Temp.	Bromine in 100 Bromine-water.	Temp.	Bromine in 100 Bromine-water.
5°C	3·600	13°	3·269	21°	3·186	29°	3·136
6	3·536	14°	3·253	22°	3·179	30°	3·131
7°	3·474	15°	3·236	23°	3·173		
8°	3·421	16°	3·228	24°	3 166		
9°	3·376	17°	3·218	25°	3·159		
10°	3·336	18°	3·208	26°	3·151		
11°	3·313	19°	3·200	27°	3·146		
12°	3·229	20°	3·192	28°	3·141		

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 16th, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society :—

John Attfield, Esq., St. Bartholomew's Hospital; J. Christian, Esq., 11, Upper Copenhagen-street, Islington; John G. Dale, Esq., Foxhill Bank, Church, near Accrington, Lancashire; Thomas L. Phipson, Esq., The Cedars, Putney; Charles W. Quin, Esq,, 4, Norman-terrace, Wellington-road, Clapham; Henry Rayner, Esq., Messrs. Chance's Chemical Works, near Oldham; Joseph Storey, Esq., Chemical Manufacturer, Lancaster; Richard Wheeler Thomas, Esq., 10, Pall Mall; C. Greville Williams, Esq., Glasgow.

The following vote of condolence was put from the chair, and carried unanimously :—

"To the Queen's most excellent Majesty,

"May it please your Majesty: We, the President, Vice-Presidents, Council and Fellows of the Chemical Society, beg permission to approach your Majesty, and humbly express our great sorrow at the death of his Royal Highness, the late Prince Consort, who during his life evinced a warm interest in the progress of the science to which our labours are devoted. We pray that the consolation and support of Almighty God may be vouchsafed to your Majesty under this severe bereavement, and that your Majesty may long continue to reign over your loyal and faithful people."

The following papers were read :—

"On the simultaneous variations of Hippuric and Uric Acids in healthy Human Urine:" by Dr. H. Bence Jones.

"On the solubility of Sulphate of Lead in Hydrochloric and Nitric Acids:" by Mr. G. F. Rodwell.

"On a new method for effecting the substitution of Chlorine for Hydrogen in Organic Compounds:" by Dr. H. Müller.

February 6th, 1862.

Dr. Frankland, Foreign Secretary, in the Chair.

Mr. John Broughton, St. Bartholomew's Hospital; Dr. Alexander Martius, and Dr. Geyger, Royal College of Chemistry, were elected Associates of the Society.

The following papers were read :—

"On Ground Ice:" by Mr. Richard Adie.

"On Crystalline Xanthine in Human Urine:" by Dr. H. Bence Jones.

"On Silica:" by Mr. A. H. Church.

"On the source of the Arsenic contained in Sulphuric Acid, and on the preparation of an Acid free from Arsenic:" by Professor Bloxam.

"On a deposit of Phosphate of Lime occurring in Teak-wood:" by Mr. F. A. Abel.

"On the composition of the Water of certain Boiling Springs in New Zealand:" by Dr. J. Smith.

February 20th, 1862.

Dr. Hofmann, President, in the chair.

Mr. Traugott Ludwig, 7, Bury-court, St. Mary-Axe, was elected a Fellow.

The following papers were read :—

"Note on Professor Bolley's paper, on some Physical Properties of the alloys of Lead and Tin:" by Dr. Matthiessen.

"On the quantitative determination of the Alkalies in Fire Clays, and other insoluble Silicates:" by Mr. G. Gore.

"On the Constitution and Artificial Formation of Taurine:" by Professor Kolbe.

"On a new source of Acetone:" by Mr. W. Valentin.

"On some transformations of Citric, Butyric, and Valeric Acids:" by Dr. Phipson.

"On the double Sulphides of Iron and Copper:" by Professor Field.

March 6th, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Thomas M. Evans, Esq., 19, Queen's-road, West, Regent's-park; F. C. Matthews, Jun., Esq., Driffield, Yorkshire; J. D. Perrins, Esq., Worcester; Thomas Alexander Pooley, Esq., 20, Great Marlborough-street.

The following papers were read:—

"On Specific Heat, in relation to Chemical Combination." by Mr. J. Croll.

"On the indifferent Hydrocarbons produced in the Destructive Distillation of Boghead Coal:" by M. C. Greville Williams.

Mr. Crace Calvert made a verbal communication upon the Action of Wood upon Iron.

Dr. Hofmann gave an account of his experiments upon the Red Colouring Matters obtained from Aniline.

March 20th, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Thomas Royle, Esq., Crayford, Kent; John Mayer, Esq., Glasgow; Leedham White, Esq., Chiselhurst, Kent.

The following papers were read:—

"On the Isolation of Phenyl:" by Mr. A. H. Church.

"On the production of a blue substance by the Electrolysis of Sulphate of Aniline:" by Dr. Letheby.

Anniversary Meeting, March 31st, 1862.

Dr. Hofmann, President, in the chair.

The following Report was read by the President:—

We have now, Gentlemen, arrived at our twenty-first anniversary. The Chemical Society has come of age. Allow me, as the delegate of your Council, to offer my sincere congratulations on this most auspicious event. Twenty-one years ago the Chemical Society, consisting then of 77 members, met, for the first time, at the rooms of the Society of Arts; to-day we assemble a chartered body, under the same roof with the Royal Society, surrounded by sister societies, with the names of 360 Fellows on our rolls.

By the number of our body, by the value of its contributions to science, by the increasing interest which our proceedings elicit, we have secured a respectable position in the world. We may look, with some degree of satisfaction, upon the achievements of our youth, and from the result of the past derive encouragement for the future.

The prosperity of the Chemical Society during the past year is well marked by the slow but steady increase of the number of its Fellows, and by the unintermittent flow of original contributions.

The present number of Fellows, as compared with the number at the last Anniversary Meeting, is as follows:—

Number of Fellows on March 30, 1861		342
Fellows elected since that date	30	
„ deceased	3	
„ resigned	1	
„ removed	8	
Increase	—	18
Present number of Fellows		360
Number of Associates on March 30, 1861		10
Associates elected since that date		4
Present number of Associates		14

Number of Foreign Members on March 30, 1861	30
Present number of Foreign Members	30

On comparing these numbers with the statistics of former years, it appears that the increase in the number of Fellows during the last twelve months is equal to that of the preceding year, and greater than the average of former years.

The three Fellows whom we have lost by death since our last anniversary, are Sir John Croft, Bart., F.R.S.; the Rev. James Cumming, M.A., F.R.S., Professor of Chemistry in the University of Cambridge, and one of the original members of the Chemical Society; and Mr. John Collis Nesbit.

Sir John Croft was born in 1778. For some years he followed the pursuit of science, especially chemistry, under Sir Humphry Davy. In 1818 he was elected a Fellow of the Royal Society, and had the honorary degree of D.C.L., conferred on him by the University of Oxford.

During the Peninsular war, and between the years 1810 and 1816, Mr. Croft was attached to the British Mission at the Court of Portugal, and, among other arduous duties, was employed by his Majesty's minister to distribute the bounty voted by Parliament, £100,000, for the relief of the inhabitants of Portugal. For this and other services he received, through Viscount Castelreagh, the approbation of the King for his conduct during the time he was entrusted with his Majesty's affairs. By the Prince Regent of Portugal he was appointed a Knight Commander of the Royal Order of the Tower and Sword, and in 1854 was created a Baron of that kingdom, under the title of Baron De Sina da Estrilla. After Mr. Croft's return to England in 1818, he was created a baronet. His early love of chemistry induced him to join the ranks of the Chemical Society soon after its formation.

The Rev. James Cumming* was born October 24, 1777. He entered the University of Cambridge in 1797, became Scholar of Trinity College in 1800, and Fellow in 1803. He graduated B.A. in 1801, obtaining honours in mathematics as tenth wrangler, and proceeded to M.A. at the usual time.

While an undergraduate, he seems to have spent much of his time in the pursuit of natural philosophy, and afterwards, for some time, used to assist Mr. Wollaston, then Professor of Natural Philosophy in the University, in his lectures and experiments. In 1815, on the death of Smithson Tennant, who was most unfortunately killed by the fall of a drawbridge at Boulogne, he succeeded to the Chair of Chemistry, and in 1819 was presented to the rectory of North Runcton, near Lynn, which had been formerly held by Maskelyne, the Astronomer Royal, and he retained both these preferments until his death. He lived frequently in Cambridge; and, though his health was never robust, he continued to give lectures every year in the University until the spring of 1860, when his course was interrupted by illness. This attack was followed by others of a more severe character, and he died on the 10th November, 1861, at his rectory at North Runcton, having just completed his 84th year.

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* I am indebted to Professor Liveing, of Cambridge, for this biographical sketch.

He retained his mental faculties to the last; and only a short time before his death he had been suggesting experiments in physical optics. His personal appearance was strikingly venerable; and his honest, independent, but unostentatious character won for him the respect of all with whom he came in contact. He was a Fellow of the Royal Society, and one of the earliest promoters of the Cambridge Philosophical Society, in which body he at one time filled the office of President.

His natural inclination seems to have led him to the pursuit of those branches of physics which are connected with chemistry, rather than to chemistry proper. Indeed, in his younger days, the sciences relating to heat and electricity were considered a part of chemistry. It was these sciences which were his favourite study, and in which most of his original work was done. In 1821 he communicated to the Cambridge Philosophical Society a paper on the application of magnetism to the measure of electricity, containing several new determinations, among which may be mentioned that of the variation due to the distance between the plates in a galvanic battery. In 1823, he communicated another on thermo-electricity—a very remarkable paper, for which he does not seem to have received due credit in the scientific world—in which he showed that electricity might be developed by the unequal heating of all kinds of conductors. He published one or two other papers of a more strictly chemical character in the Transactions of the same society, and also a Manual of Electrodynamics (Cambridge, 1827). In his lectures, the branches of physics already mentioned had always a prominent place; and it was remarkable how quickly he seized the point, and how clearly he expounded the bearings, of new discoveries in science. In 1820 he exhibited in his lectures Oersted's famous experiment; and, as more than one of his auditors bears witness, he pointed out at the time how in these experiments might be traced the principle of an electric telegraph. His skill in manipulation was equal to the clearness of his expositions. An experiment in his hands rarely failed; and as his Professorship was not furnished with any apparatus, almost the whole of his physical apparatus was constructed with his own hands.

To the last he kept himself *au courant* in matters of science; and as soon as new processes for preparing aluminium had placed that metal within his reach in sufficient quantity, he proceeded to determine its qualities in regard to electricity. He made altogether very many determinations of this kind, which, if he had been at all ambitious of distinction, would have been well worthy of publication.

John Collis Nesbit was born at Bradford in 1819. He was brought up at Manchester, where his father—the author of several much esteemed mathematical school-books—conducted a large private school. The son's attachment to chemistry was manifested very early in life, and was not to be subdued by the discouragement of his friends. Having, at the age of fifteen, constructed a variety of philosophical instruments, including an electric battery, which was purchased for 30 guineas by the Manchester Mechanics' Institution, and having afterwards delivered several lectures at that Institution, his wishes were no longer thwarted, and he was placed under the guidance of the celebrated Dr. Dalton.

When barely of age, he removed to London, and devoting his attention chiefly to chemistry in relation to agriculture, established at Kennington his College of Chemistry and Agriculture, for the instruction of youths in natural and applied science, and became well known throughout the country as a lecturer on agricultural chemistry, succeeding well in illustrating his subject and in interesting his audience.

Mr. Nesbit was the author of treatises "On the Analysis of the Hop;" "On Peruvian Guano;" "On the History and Properties of the different varieties of Natural Guanos;" and of a "Course of Lectures on Agricultural Chemistry." He was elected a Fellow of this Society in 1845, and communicated several papers which appeared in the earlier volumes of the Society's

Journal. He was also a Fellow of the Geological Society. He recognised the presence of phosphoric acid in the Farnham marls, and contributed to the Exhibition of 1851 a collection of fossil phosphates, which received honourable mention. In 1856, he pointed out to the French Government the positions of numerous beds of coprolites which he had discovered in that kingdom. In 1857 he was presented, by the Central Farmers' Club, with a testimonial, consisting of a service of plate and a Ross's microscope, in acknowledgment of the benefit which the agricultural community had received from his chemical labours, and especially from his successful endeavours in detecting and exposing the adulteration of manufactured and imported manures.

During the latter part of his life Mr. Nesbit suffered much from failing health, and died on March 30, after a lingering illness, æt. 42.

The papers communicated to the Chemical Society and read at our meetings, and the discourses delivered since our last anniversary, are not less varied and interesting than those of former years. The contents of the papers and discourses, which have nearly all appeared in our Journal, being still fresh in your memory, I may limit myself here to recording their titles.

List of Papers read at the Meetings of the Chemical Society, from March, 1861, to March, 1862 :—

1. "On some Derivatives from the Olefines:" by Dr. Frederick Guthrie.
2. "On the Action of Dibromide of Ethylene upon Pyridine :" by T. Davidson, Esq.
3. "On the amount of Water displaced from the Hydrates of Potash, Soda and Baryta, by Boracic and Silicic Acids :" by Professor Bloxam.
4. "On the Graphite of Cast-iron :" by Professor Crace Calvert.
5. "On Bromide of Carbon," by A. E. W. Lennox, Esq.
6. "On the power ascribed to the Roots of Plants of rejecting Poisons or other Abnormal Substances presented to them :" by Dr. Daubeny.
7. "On the Constitution of Gastric Juice :" by Dr. Marcet.

8. "On the Action of certain Gases upon the Peroxides of Potassium and Sodium:" by A. Vernon Harcourt, Esq.
9. "On some results of the Analyses of Commercial Copper:" by Messrs. Abel and Field.
10. "On the occurrence of Bismuth in various descriptions of Copper ore:" by F. Field, Esq.
11. "On Leucic Acid, and some of its Salts:" by Dr. Thudichum.
12. "On the occurrence of Crystalline Deposits of Phosphate of Lime in human Urine:" by Dr. H. Bence Jones.
13. "On Sparteine:" by E. J. Mills, Esq.
14. "On Peppermint Camphor:" by Dr. Oppenheim.
15. "On Piperic and Hydropiperic Acids:" by G. C. Foster, Esq.
16. "On Supplementary Experiments upon the power ascribed to the Roots of Plants of rejecting Poisons and Abnormal Substances presented to them:" by Dr. Daubeny.
17. "On some Physical Properties of Tin-lead Alloys:" by Professor Bolley.
18. "On the Dangers arising from the use of certain Waters for feeding Steam-boilers:" by Professor Bolley.
19. "On the Simultaneous variations in the amounts of Hippuric and Uric Acids excreted in healthy Human Urine:" by Dr. H. Bence Jones.
20. "On the Solubility of Sulphate of Lead in Hydrochloric and Nitric Acids:" by Mr. G. F. Rodwell.
21. "On a new method for effecting the substitution of Chlorine for Hydrogen in Organic Compounds:" by Dr. H. Müller.
22. "On Ground Ice:" by Mr. Richard Adie.
23. "On Crystalline Xanthine in Human Urine:" by Dr. H. Bence Jones.
24. "On Silica:" by Mr. A. H. Church.
25. "On the Source of the Arsenic contained in Sulphuric Acid, and on the preparation of that Acid free from Arsenic:" by Professor Bloxam
26. "On the deposit of Phosphate of Lime occurring in Teak Wood:" by Mr. F. A. Abel.
27. "On the Composition of the Water of certain boiling springs in New Zealand:" by Dr. J. Smith.
28. "Note on Professor Bolley's paper on some Physical Properties of the Alloys of Lead and Tin:" by Dr. Matthiessen.
29. "On the Quantitative Determination of the Alkalies in Fireclays, and other Insoluble Silicates:" by Mr. G. Gore.

30. "On the Constitution and Artificial Formation of Taurine:" by Professor Kolbe.
31. "On a new source of Acetone:" by Mr. W. Valentin.
32. "On some transformations of Citric, Butyric, and Valeric Acids:" by Dr. Phipson.
33. "On the double Sulphides of Iron and Copper:" by Mr. F. Field.
34. "On Specific Heat in relation to Chemical Combination:" by Mr. J. Croll.
35. "On the indifferent Hydrocarbons produced in the Destructive Distillation of Boghead Coal:" by Mr. C. Greville Williams.

List of Discourses delivered at the Meetings of the Chemical Society:—

1. "On the application of Electricity to the Explosion of Gunpowder:" by F. A. Abel, Esq.
2. "On the Colouring Matters obtained from Coal Tar:" by W. H. Perkin, Esq.
3. "On the application of the Induction-coil to Steinheil's apparatus for Spectrum-analysis:" by Dr. H. E. Roscoe.

The communications made to the Chemical Society illustrate, in a measure, the activity with which all the different branches of Chemical Science have been cultivated during the last year. To present to the Society a sketch of the progress of Chemistry during the last twelve months, even were it traced in the merest outlines, would be outstepping the legitimate limits of this report, I must, therefore, be satisfied to single out of the vast number of valuable materials diffused in the periodical literature of the year, a few of the researches which appear to me to claim particular attention. On the boundary line between Physics and Chemistry, we meet with Magnus' Researches on the Temperature of the Vapour of Saline Solutions, which both in method and result, are intimately connected with Faraday's earlier investigations; Tyndall's experiments on the Absorption and Radiation of Heat by Gases and Vapours, and on the Physical connection of Radiation, Absorption and Conduction; and Dufour's observations on the preservation of the Liquid condition. The harvest of results in Mineral Chemistry has been particularly rich; I need only refer to the remarkable researches on Dialysis, communicated by one of our colleagues to the Royal Society, which open a new page in Chemical Analysis, and to the beautiful experiments on the influence of Pressure on Combustion, which were contributed by another. The wonderful discoveries of Bunsen and Kirchhof have been chiefly published in the previous year, but the further elaboration of the two new metals Caesium and Rubidium by Bunsen, belongs to the finest fruits which the last year has ripened. The method of spectral analysis, established by the researches of the two German philosophers, cannot fail to exercise a powerful influence upon the direction of chemical inquiry during the ensuing decade. Already we possess, in the important discovery of another new element, Thallium, announced by one of our colleagues, an additional earnest of what we may expect from the continuation of these researches. Among the important results obtained in the department of Inorganic Chemistry, Deville's remarkable experiments upon the reproduction of minerals must not be forgotten. The controversy between Fremy and Caron, respecting the composition of steel, has not yet been finally settled; but the interest attached to the question is unequivocally manifest from the number of observers whom it has called into the field. Even more numerous have been the labours in the domain of Organic Chemistry. The researches of Wurtz on Oxide of Ethylene; of Cahours on the Alcohol-radicals; the interesting experiments of Kekulé on Organic Acids; of Strecker, on Guanine and collateral matters; of Griess, on Nitrogen substitution; the animated discussion on the constitution of Lactic Acid, between Wurtz and Kolbe; the synthesis of Succinic Acid by Simpson, etc.; have materially contributed to accelerate the progress of Organic Chemistry. Again, I must not leave unnoticed, Pasteur's remarkable inquiries into the nature of fermentation, although the chief results of this investigation belong to a previous period. Nor would it be right to bring this very imperfect sketch to a conclusion, without alluding to the important contributions to Chemical Literature, which the last year has witnessed. Dr. Miller's excellent work on Chemistry has gone through a new edition, and the chemical student has welcomed with pleasure the first parts of two long-expected books, Dr. Odling's "Manual of Chemistry," and Dr. Percy's "Metallurgy."

The unprecedented activity which prevails in the several departments of Chemistry, and in the collateral sciences, has induced your Council to devote particular attention to the facilities of publication which the Society has hitherto been enabled to hold out to contributors. During the first six or seven years of its existence, the Chemical Society published the papers read at its meetings, in numbers appearing at irregular intervals. The papers thus published, constitute the three volumes of "Memoirs and Proceedings of the Chemical Society of London," 1841 to 1848.

In the latter year, the Memoirs and Proceedings were replaced by the "Quarterly Journal of the Chemical Society;" and in order to make this Journal more useful to the members and acceptable to the public, it was resolved, that notices of all important papers upon Chemical subjects, published in foreign journals, should be appended to each number; and further, that the January number of each year, should contain an alphabetical list of the heads of all chemical papers published during the year, both at home and abroad, up to the time of the publication of the Journal.

In strict accordance with these resolutions, the Quarterly Journal of the Chemical Society was published up to the year 1860, when it was found convenient to discontinue the alphabetical list of the heads of Chemical papers. In fact, this list, which when first published, occupied not more than nineteen or twenty pages, had gradually expanded beyond legitimate proportions, filling in the last volume in which it appeared, not less than 79 pages, or one-quarter of the whole volume. By its discontinuance, a considerable amount of additional space was thus given for original communications and for abstracts, but it proved inadequate to the requirements of the Society. In 1860 and 1861 the improvement of the Journal had been repeatedly under the consideration of the Council; who ultimately decided that the Quarterly Journal should be replaced by a Monthly Journal, each number to contain two and a-half sheets, whereby the annual volume will be raised from twenty-four to thirty sheets. The rank a society holds will always depend upon the number, value, and rapidity of its publications. I believe, therefore, that the transition from a quarterly to a monthly journal will be received with general approbation. Not only does this change secure to our contributors almost immediate publication, but it will enable us also henceforth to publish abstracts of all valuable chemical papers which are dispersed in the Proceedings and Transactions of the several learned societies, in which they are not always easily accessible, and to make our journal a sort of *Compte Rendu* of all the work done in chemical science throughout the country.

I now call upon you, gentlemen, to proceed to ballot for the officers of the ensuing year. The Secretary will then read some of the Bye-laws which have been revised by your Council, various alterations having suggested themselves by the experience of the ten years which have elapsed since the Bye-laws were last under your consideration in 1852. Printed copies of the revised Bye-laws are upon the table; I trust that the alterations will meet with your approval and receive your sanction.

The meeting then proceeded to elect the Council and Officers for the ensuing year, and the following were declared to have been duly elected:—

President.—A. W. Hofmann, Ph.D., L.L.D., F.R.S.

Vice-Presidents who have filled the office of President.—W. T. Brande, F.R.S., B. C. Brodie, F. R. S., C. G. B. Daubeny, M.D., F.R.S., Thomas Graham, F.R.S., W. A. Miller, M.D., F.R.S., Lyon Playfair, C.B., F.R.S., Col. Philip Yorke, F.R.S.

Vice-Presidents.—H. Bence Jones, M.D., F.R.S., Alfred Smee, F.R.S., A. W. Williamson, F.R.S., Robert Warington.

Secretaries.—T. Redwood, Ph.D., W. Odling, M.B., F.R.S.

Foreign Secretary.—E. Frankland, Ph.D., F.R.S.

Treasurer.—Warren De la Rue, Ph.D., F.R.S.

Other Members of Council.—F. A. Abel, F.R.S., Thomas Andrews, M.D., F.R.S., William Francis, Ph.D., F.L.S., J. H. Gladstone, Ph.D. F.R.S., J. B. Lawes, F.R.S., G. H. Makins, A. Matthiessen, Ph.D., F.R.S., A. Normandy, W. H. Perkin, H. E. Roscoe, Ph.D., Edward Schunk, Ph.D., F.R.S., John Stenhouse, L.L.D., F.R.S.

Some alterations in the Bye-laws, duly sanctioned by the Council, having been submitted to the meeting,

It was moved by Dr. Odling, seconded by Mr. Warington, and resolved—

"That the existing Bye-laws be abrogated and annulled, and that the following be the Bye-laws of the Chemical Society:"—

[These Bye-laws are published separately.]

It was moved by Professor Faraday, seconded by Mr. Makins, and resolved—

"That the thanks of the meeting be given to the President and Council for the services rendered to the Society during the past year."

THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON.

Drs.

		£ s. d.	£ s. d.
1861. March 25.	To Cash in hand		569 11 10
1862. March 11.	„ Half-yearly Dividend on £500 3 per cent. Consols		7 4 5
	„ „ „ on £600 „ „		8 13 3
	„ Sundry Receipts from March 25th, 1861, to March 25th, 1862, as below:—		
	Life Compositions	59 0 0	
	Admission Fees	64 0 0	
	Resident Members' Subscriptions previous to 1861	10 0 0	
	Non-resident Members' Subscriptions previous to 1861	4 0 0	
	Resident Members' Subscriptions for 1861	72 0 0	
	Non-resident Members' Subscriptions for 1861	23 0 0	
	Resident Members' Subscriptions for 1862	272 0 0	
	Non-Resident Members' Subscriptions for 1862	92 0 0	
			596 0 0
		£	1181 9 6

Crs.

		£ s. d.	£ s. d.
1861. Journal.	By Editor's Salary to 25th March, 1862	80 0 0	
	„ Printing Journal	202 19 11	
	„ Distributing Journal	7 16 0	
			290 5 11
Library.	„ Librarian's Salary to 25th March, 1862	25 0 0	
	„ Proceedings of the Royal Society	50 0 0	
	„ Books and Magazines	27 0 0	
	„ Bookbinding	8 18 2	
			110 18 2
Collector and Clerk.	„ Collector's Commission	29 16 0	
	„ Clerk	3 0 0	
			32 16 0
Stationery, Postage, &c.	„ Account Book, Postage, Envelopes, Receipt Stamps, &c.	6 1 4	
	„ Draft Stamps	0 4 0	
	„ Carriage of Books, Stationery, &c.	1 12 2	
	„ Engrossing Address to Her Majesty	0 5 0	
			8 2 6
House Expenses.	„ Royal Society, Share of Expenses for Refreshments	15 18 9	
	„ Thos. Hux, Salary to 25th March, 1862	20 0 0	
	„ „ (as per book), Gas, Oil, &c.	1 14 0	
	„ „ „ Glazing, Painting, &c.	1 4 6	
	„ W. Page, Cleaning	1 1 0	
	„ Gate Porter, Christmas Gratuity	1 1 0	
			40 19 3
Furniture.	„ Balloting Boxes (R. Ireland)	10 10 0	
			10 10 0
	„ Purchase of £100 3 per cent. Consols	90 0 0	
			90 0 0
June 13.	„ Balance at Messrs. Coutts and Co.	556 17 8	
	„ „ in Cash in hands of Treasurer	41 0 0	
			597 17 8
		£	1181 9 6

Assets.	£ s. d.
Balance in Cash	597 17 8
Invested in 3 per cent. Consols	600 0 0
	£1197 17 8

Examined and found correct,

PHILIP J. CHABOT,
GEORGE GLADSTONE,
W. H. THORNTHWAITE,
} *Auditors.*

London, March 26th, 1862.

April 3rd, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Alfred Sidebottom, Esq., Crown-street, Wyndham-road, Camberwell; C. Haughton Gill, Esq., 52, Chancery-lane; William Symons, Esq., 17, St. Mark's-crescent, Regent's-park.

Dr. Debus delivered a discourse—"On the Influence of the Quantitative Method on the Development of Scientific Chemistry."

April 17th, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellow of the Society:—

Dr. Julian Courtauld, Braintree, Essex; Dr. C. M. von Bosé.

The following paper was read:—

"On the Action of Carbonate of Ammonium on Magnesian Salts:" by Dr. Edward Divers.

May 1st, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Peter Spence, Esq., Pendleton Alum Works, Manchester; Charles Graham, Esq., Berwick-upon-Tweed; H. G. Madon, B.A., Queen's College, Oxford; W. Esson, B.A., Merton College, Oxford.

Dr. Thomas Anderson delivered a discourse—"On the the Chemistry of Opium."

May 15th, 1862.

Dr. Hofmann, President, in the chair.

M. H. St. Claire Deville delivered a discourse—"On Vapour-densities."

May 29th, 1862.

Thomas Graham, Esq., Vice-President, in the chair.

The following papers were read:—

"On the Action of Mordants upon Cotton-fibre:" by Walter Crum, F.R.S.

"On the Capacity of Arsenious Acid for Bases and on certain Arsenites:" by Professor Bloxam.

Additional notes—"On Reciprocal Decomposition among Salts in Solution:" by Dr. Gladstone, F.R.S.

"On the General Occurrence of Titanic Acid in Clays:" by Mr. E. Riley.

June 5th, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Charles Low, Junr., Esq., 3, St. James's-road, Holloway; Fernside Hudson, Esq., Laboratory, Corporation-street, Manchester.

Professor Wurtz delivered a discourse—"On Oxide of Ethylene, considered as a link between Mineral and Organic Chemistry."

June 19th, 1862.

Walter Crum, Esq., in the chair.

Messrs. Cannizzaro, Kekulé, Loewig, Malaguti, Marignac, Pasteur, Stas, and Zinin, were elected Foreign Members of the Society.

Dr. Marcet delivered a discourse—"On the Chemistry of Digestion."

The following papers were read:—

"On Berberine, contributions to its history, and revision of its formula:" by Mr. W. D. Perrins.

"On the Formation of Iodides of the Alcohol-radicles from Boghead Naphtha:" by Mr. C. Greville Williams, F.R.S.

November 6th, 1862.

Dr. Hofmann, President, in the chair.

F. A. Bowman, Esq., of Halfax, was elected a Fellow of the Society.

The following papers were read :—

"On the Separation of Tin from Antimony, and on the Analysis of Alloys containing Lead, Tin, Antimony, and Copper:" by Charles Tookey, F.C.S.

"On a Volumetric Process for the Analysis of Water:" by E. Nicholson, F.C.S.

A note from Professor Heintz to Dr. H. Bence Jones—"On the Composition of the Amorphous Deposit in Healthy Urine," was next read.

"On Hypobromous Acid:" by William Dancer.

November 20th, 1862.

Dr. Hofmann, President, in the chair.

W. G. Blagden, Esq., was elected a Fellow of the Society.

The following papers were read :—

"On the Formation of Organo-metallic Radicles by Substitution:" by G. B. Buckton, Esq.

"On the Specific Gravity of Urine as a measure of its solid Constituents:" by E. Nicholson, Esq.

Dr. Hofmann demonstrated the Properties of the Spontaneously Inflammable Silicated Hydrogen Gas, discovered some time back by Buff and Wöhler.

December 4th, 1862.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society :—

George Farrer Rodwell, Esq., 15, Great Marlborough-street; G. W. Septimus Piesse, Esq., 2, New Bond-street; Thomas

Farmar Hall, Esq., Kennington; William Gossage, Esq., Widness, near Warrington; John Chapman Wilson, Esq., Making Place Hall, near Halifax; James Richards, Esq., Clifton Lodge, near Preston, Lancashire; Magnus M. Tait, Esq.; W. H. Michael, Esq., M.R.C.S., Northwich, Harrow.

John Henry Baldock, Esq., 55, St. James's road, Holloway, was elected an Associate of the Society.

The following papers were read:—

"Notes on certain Processes of Rock-formation:" by Mr. Arthur H. Church.

"On the Determination of the amount of Organic Matter in Drinking Water by means of a Standard Solution of Permanganate of Potash:" by Dr. Woods.

"On the effect of Heating Sulphate and Sulphide of Lead in Hydrogen and Carbonic Oxide:" by Mr. G. F. Rodwell.

"On the Composition of Gall-stones:" by Dr. Thudichum.

December 18, 1862.

Dr. Hofmann, President, in the Chair.

Messrs. W. A Dixon, John Hooker, Alexander Taylor Machattie, and Edmund James Mills, were elected Fellows.

Dr. Frankland gave an account of some experiments made by Messrs. Wanklyn and Erlenmeyer on Hexylic Alcohol.

Mr. Field read a note—"On the Solvent Power exercised by a Solution of Hyposulphite of Soda upon many Salts insoluble in Water."

Donations to the library received in the year 1862:—

"On the Physical Forces concerned in the Phenomena of Vegetation:" by C. Daubeny, M.D., F.R.S.: from the Author.

"On the Concrete used in the late Extension of the London Docks;" by George Robertson, C.E.: from the Author.

"*Vis inertia victa*, or Fallacies affecting Science:" by James Reddie: from the Author.

"Researches on the Solar Spectrum, and the Spectra of the

Chemical Elements:" by G. Kirchhof: translated by H. E. Roscoe: from the Translator.

"Chemical Contributions to Silliman's Journal:" by M. Carey Lea: from the Author.

"Notes on the Chinese Materia Medica:" by Daniel Hanbury: from the Author.

"On the Sources of the Nitrogen of Vegetation:" by J. B. Lawes, J. H. Gilbert, and Evan Pugh: from the Authors.

"Fifth Report on Experiments on the Feeding of Sheep:" by J. B. Lawes and J. H. Gilbert: from the Authors.

"The Sulphureous Bath at Sandefiord, in Norway:" by Drs. Ebbesen and Hörbye: from the Authors.

"The Chemistry of Soils:" by Dr. Scoffern: from the Author.

"Gold-mining and the Gold Discoveries made since 1851:" by J. A. Phillips: from the Author.

"Contents of the Correspondence of Scientific Men of the Seventeenth Century:" by Augustus De Morgan: from the Author.

"Anasthesia, considered especially in reference to operations in Dental Surgery;" by A. Coleman: from the Author.

"On a Series of Organic Compounds containing Boron:" by Dr. E. Frankland: from the Author.

"A Dictionary of Calico-printing and Dyeing:" by Charles O'Neill: from the Author.

"Results of the Meteorological Observations made under the direction of the United States' Patent Office and the Smithsonian Institution, from 1854 to 1859 inclusive, being a Report of the Commissioner of Patents, made at the first session of the 36th Congress, Vol. I:" from the Smithsonian Institution at Washington.

"Smithsonian Miscellaneous Collections," Vols. I to IV: from the Smithsonian Institution.

"Report of the Commissioner of Patents (U.S.) for the year 1861:" from the Agricultural Commissioner.

"Circular from the Commissioner of Agriculture (U.S.) on the present Agricultural, Mineral, and Manufacturing Condition and Resources of the United States:" from the Commissioner.

"On the rolling and Casting of Metals:" by J. Tylor, Esq.: from the Author.

"Statistical notes of the progress of Victoria, from the foundation of the Colony:" First series, Parts 1, 2 (1835—1860): by W. H. Archer,

"Statistical Register of Victoria, from the foundation of the Colony, with an Astronomical Calendar for 1855:" edited by W. H. Archer.

"The Victorian Government Prize Essays:" (1860.)

"Catalogue of the Victorian Exhibition of 1861, with Prefatory Essays;" by W. H. Archer and others.

"The Catalogue of the Melbourne Public Library" for 1861.

"Essais divers servant d'introduction au Catalogue de l'Exposition des Produits de la Colonie de Victoria: par W. H. Archer, &c.

Die Colonie Victoria in Australien, ihr Fortschritt, ihre Hülfsquellen, und ihr physikalischer Charakter, in Abhandlungen von W. H. Archer:

from the Council of the University of Melbourne.

"Dictionnaire de Chimie Industrielle;" par MM. Barreswil et Girard, Tome II, Pt. 1: from the Authors.

"Estudios quimicos sobre el Aire Atmosferico de Madrid;" por D. Ramon de Luna: from the Author.

"Lecciones Elementares de Quimica Géneral," Tomos I, II; por Don R. Torres Muñoz de Luna: from the Author.

"Zum Gedächtniss an Jean Baptiste Biot (gesprochen in der öffentlichen Sitzung der königl.-bayer. Akademie der Wissenschaften, am 28 März, 1862):" von Carl. F. Ph. von Martius.

"Denkrede auf Gotthilf Heinrich v. Schubert:" von Dr. Andreas Wagner:

from the Royal Bavarian Academy of Sciences.

Periodicals:—

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ERRATA.

Page 394, foot-note, *for* Methode de Chemié *read* Méthode de Chimie.

Page 396, line 6 from bottom, *for* diethlyic *read* diethylic.

„ 402, „ 3 from bottom, *for* chloraceten, *read* chloracetin.

„ 408, „ 5 from top, *dele* "four."

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